

A MULTIPLE TRACER APPROACH TO DETERMINE THE GROUND AND
SURFACE WATER RELATIONSHIPS IN THE SOUTHERN MARIA DE LIGA RIVER,
COLUMBIA COUNTY, FLORIDA

By

ROBERT A. ROBERT

A DEDICATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1994

ACKNOWLEDGEMENT

I would like to thank my committee members for encouraging and supporting me throughout this endeavor and especially Mr. Riles for providing me the facilities needed and support for pursuing this study as well as her numerous editorial comments. In addition, I would like to acknowledge that many of the tools and methods in this work closely follow the guidelines and advice, both written and verbal, of Mr. R.E. Riles. I am forever indebted to Dr. Riles for all of his help in the lab and in the field with this project. His friendship and advice are truly genuine. Thanks are also extended to the numerous students who spent many hours of sleep and helped with the field experiments in this study. My sincere thanks go to the excellent staff at Oregon State Park, especially its manager Mr. Dale Hendrick for all of his help. I also thank the National Science Foundation, Geological Society of America and Sigma Xi for providing funds for this project. Also, I would like to thank the staff of the University Statistics Association for their assistance through this project.

Finally, I thank my sisters Tricia, Barbara, Vicki and Terri and my parents Gerald and Karen for their never ending support and encouragement in all my endeavors. Hopefully

they write, this will be my last academic year. Lastly I would thank my wife, Winski, for helping me through all the tough times and laughing with me during all the good ones.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	iii
LIST OF TABLES	viii
LIST OF FIGURES	ix
ABSTRACT	xii
CHAPTER	
i. INTRODUCTION	1
PURPOSE	1
Significance	1
Study Area	2
Physiography	2
Climate	3
Geology	3
Soils	4
Vegetation	4
Regional Ground Water Flow	5
Water Resources	5
ii. BACKGROUND	11
Geology	11
Soil	12
Water Resources	12
Watershed	13
Geopressure	13
Cation Concentration	13
Ground Hydrogeological Survey Locations	14
Groundwater Quality Locations	14
iii. MATERIALS AND METHODS	15
Gas Chromatography and the Injection Port	15
GC/MS	17
The Injection System	17
Thermometry	17
Sampling Techniques	18
Site Sampling	18
Modulating the Sample	18

Barium-Based Log	42
Copper-113-Based Log	43
Cation Exchange	43
Quality Control	43
Sample Preparation Methods	43
Analyses	43
X-ray Fluorescence	43
X-ray Diffractometry	43
X-ray Spectroscopy	43
Infrared Spectroscopy	43
Raman Spectroscopy	43
Nuclear Magnetic Resonance	43
Mass Spectroscopy	43
Thermal Analysis	43
Atomic Absorption Spectroscopy	43
Computer Modeling	43
Numerical Models	43
4. METHODS AND DISCUSSION	74
Mining Experiments	75
Introduction	75
Benton-113	75
Barium-Based Clay	75
Synthesis of Bentonite and Mining	75
Injection of Bentonite Suspensions	75
No Lignosulfite Bentonite	76
Lime Slime to Ten Billionths	76
Lime Slime to Calcium Suspensions	76
Summary of Mining Experiments	76
Lignite Suspensions	76
No Lignosulfite Bentonite	76
Lime Slime to Ten Billionths	76
Lime Slime to Calcium Suspensions	76
Discussion	76
Water Treatment Experiments	76
Lignite Slime to River Slime	76
Bentonite	76
Bentonite to Sludge to River Slime	77
Lime Slime to Sludge to River Slime	77
Summary of Water Treatment	77
Flow-Through Analysis	78
Benton-113 Treatment	78
Solid Treatment	78
Cation Concentrations	79
Temperature Treatment	79
Computer Modeling	79
Retention Studies	79
One-Two-Three-Flow	79
Assumptions	79
5. SUMMARY AND CONCLUSIONS	127
Mining	128
Treatment	128
Flow Components	128
Retention	128

INTRODUCTION	300
Kern Development In Other States	307
APPENDICES	
A GAS CHROMATOGRAPH AND THE INJECTION PORT SYSTEM	373
B INJECTION SYSTEM	383
C CATION BOTTLE PREPARATION	397
REFERENCES	409
DISCUSSION	411

LIST OF TABLES

Table	Page
1. Required thicknesses in Northeastern Missouri County, route 66 corridor, 1990	19
2. Applicable convertibility of natural stone aggregate to other mineral fillers	24
3. Applicable base for stone mixtures throughout the stone Corporation	32
4. Selected size until passing size of three River Stone Size	33
5. Selected Passage Size for the River Stone at Rock Hill	33
6. Travel Plans for SP-1 in Miles in O'Lake State Park	33
7. SP-1 Travel Plans for stone size to tents in River Stone Department	33
8. Certain concentrations for densities in O'Lake State Park	33
9. Approx. drying date for the River Stone	33
10. Values of k in N/mm per day for intervals between the storage drying densities in the Sand Research Station	34
11. Values of k in N/mm per day for intervals between the storage drying densities in the Sand Research Station	35
12. Comparison of relative numbers for SP-1, SP-100, and SP-11 selected temperatures	35
13. Comparison of selected stone properties (quartzite) before and through the use of volatile fumes	35

LIST OF FIGURES

FIGURE	PAGE
1. Santa Fe River Basin in north-central Florida (after RUM and BLACK, 1983).....	1
2. Springs found in western Santa Fe River Basin, (after RUM and BLACK, 1983).....	1
3. Potentiometric surface of the Floridan aquifer and direction of ground water flow in the study area (from RUM, 1992).....	10
4. Hydrogeologic provinces in the study area (from KLEINER, 1994).....	11
5. Hydrologic features in peninsular North Florida (after HEDDERSON, 1993).....	14
6. Geology of western Santa Fe River Basin (after RUM, 1983).....	19
7. Cross section through the western Santa Fe River Basin (after RUM, 1983).....	19
8. Hydrogeologic units of the western Santa Fe River Basin (after RUM and BLACK, 1983).....	20
9. Rio Grande as natural Re-OH ₂ concentration (from KELLY et al., 1990).....	40
10. Subducting River Re-OH ₂ concentrations.....	41
11. Charcoal particle used in rhythmite age dating experiments.....	50
12. Sampling device and graduated cylinder for SP4 and Re-OH ₂	62
13. Rises to plateau for SP4 in the western Santa Fe River.....	65
14. a. Rhythmite thickness grid; b. Computer program for rhythmite thickness grid (after RUM, 1992).....	66

16.	Lower Santa Fe River Basin near Glendo Springs (Brown Ellerbe et al., 1992).....	63
17.	Sample locations at Goldingsmouth Ranch (Myers Ellerbe et al., 1992).....	63
18.	River sites to 4 km on Lower Santa Fe River (Brown Ellerbe et al., 1992).....	65
19.	Flow reduced to Glendo Springs on Lower Santa Fe River (Brown Ellerbe et al., 1992).....	67
20.	60 ^o concentration response curves 0.3 to 1.0 mg/L.....	68
21.	60 ^o concentration response curves 0.3 to 0.5 mg/L.....	69
22.	Unadjusted concentrations of ^{226}Ra concentrations in river near Goldingsmouth Ranch (Brown Ellerbe et al., 1992).....	70
23.	Mining results at 0.5, 1.0, 1.5 km downstream of the River Mine.....	70
24.	Glendo State Park with numbered sample locations for Glendo Ranch experiment (Brown Ellerbe et al., 1992).....	122
25.	Geology of Glendo Mine.....	125
26.	Geology of River Mine.....	126
27.	Concentration response curves for Ogallala Park, Burke Ranch, Paradise Ranch Mine and South Mine.....	128
28.	Concentration response curves for New Mine, Ogallala Mine, Two Mine and Sweetwater Lake.....	129
29.	Concentration response curves for Sweetwater Mine.....	129
30.	Concentration response curves for Ogallala Mine experiment.....	130
31.	Concentration response curves for Ogallala Mine experiment.....	131

3.2	Flow Patterns of the ungauged areas, Pa River through Cruse State Park	124
3.3	Sample locations for ^{238}U , ^{232}Th , major elements and temperature	127
3.4	Activity- ^{238}U concentrations for karst features found throughout the park	128
3.5	$\delta^{18}\text{O}$ Values for Karst Features in Cruse State Park	130
3.6	CaCO ₃ Concentrations in Cruse State Park	130
3.7	Temperature Readings Recorded at Cruse State Park	130
3.8	Computer model set up for the western state Pa River region between Cruse State Park and New Salem	132
3.9	Sampling locations for the first reservoir experiment	136
3.10	Bottom concentrations and water profiles for the first reservoir experiment	137
3.11	Sampling locations for the second reservoir experiment	149
3.12	Bottom concentrations and water profiles for the third reservoir experiment	150
3.13	Gas chromatograph setup for ICP analysis	170
3.14	Three sections of discrete holes used in the analysis	172
3.15	Mixed pore injection system for ICP analysis	179
3.16	Silicon syringe used for injecting ICP samples	180
3.17	Gas mixed injection system used throughout all injection experiments	180

ABSTRACT OF DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
AT THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

A MULTIPLE TRACER APPROACH TO DETERMINE THE SOIL/WATER AND
WATER/WATER RELATIONSHIPS IN THE WATERSHED FROM THE RIVER,
ORLANDA COUNTY, FLORIDA.

By
Richard A. Smart

December 1984

Chairman: Douglas L. Smith
Major Department: Geology

This project characterized the complex karstic groundwater/surface water relationships of the Santa Fe River in north-central Florida while further developing the use of the new geochemical tracer sulfur hexafluoride ($^{18}\text{SF}_6$) and neutrally conserving tracer- ^{87}Rb (^{87}Rb) as well as relatively established hydrologic techniques. To accomplish the objectives, mixing, tracer tracing, flow component and retention experiments were conducted along several reaches of the Santa Fe River and within Orange State Park.

The mixing experiments revealed the effects of branching springs and seepage within the stress cross section and suggested more detailed sampling descriptions in order to accurately evaluate stress parameters. In addition, these experiments established nearly developed SF_6 injection

techniques. Other tracing experiments established two things: 1) SF_6 is an excellent tracer for surface and ground water tracing and 2) the breakthrough using tracer amounts is within three days.

The component analysis further described the complex water balance within SF_6 tracer breakthrough comparing several techniques. Directly, retention studies confirmed the usefulness of SF_6 in determining the pathways to karstic discharge sites.

A continuation of the research was the establishment of a tracer-trace SF_6 analytical laboratory, one of only a handful in North America. SF_6 has become a viable alternative to the presently used dye and harmful gases, perhaps one of the most complete ground water and surface water tracers in the world. In addition, because this study was undertaken successfully in such a hydrologically complicated environment, future use of SF_6 in simpler environments promises to be successful as well.

CHAPTER 1 INTRODUCTION

The nature of native karst regions is complex and hydrogeologically difficult to describe. Close to the historical development of a karst region are also hard to estimate. Both studies of karst regions employ a variety of hydrogeologic tracers that were often selected mainly inadequate and negative side effects (Mauri, 1999). As karst regions, in general, become increasingly populated the need to develop a reliable and environmentally safe ground and surface water tracer is obvious (Garcia-Prado, personal communication, 1994). Other tracers, like a newly developed artificial tracer, provide a means to integrate ground and surface water interactions in a dependable, non-toxic manner.

Related areas found within this region of Florida are possible ones except to the geological development of karst, both past and present. The natural study of karst and related areas together may aid in the future planning of active karst regions. The Santa Fe River Basin in north-central Florida provides the unique opportunity to assess the relationship between ground water and river water and wetlands within a complex karstic setting.

Objectives

The primary purpose of this project was to accurately characterize the complex borehole ground water/surface water relationships of the Santa Fe River while continuing to develop the use of the two spatiotemporal tracer ^{87}Rb and naturally occurring ^{87}Sr . The relationships between the two primary water resources, ground water and surface water, were assessed in terms of their distribution using ^{87}Rb , ^{87}Sr and other tracing techniques. The watersheds in the region were also addressed in terms of their chemical signature and connection between ground and surface water. In order to accomplish this task several goals were outlined. They included:

- 1) developing and developing an efficient laboratory, logistics system and collection system for the disposal and analysis of ^{87}Rb ,
- 2) understanding the temporal changes of the Santa Fe River system,
- 3) understanding the mixing aspect of the river,
- 4) characterizing ground water, surface water and spring water (^{87}Sr concentrations) in the study area,
- 5) develop and if not all, subsurface flow regimes and links of ground water to the Santa Fe River within the O'Leno State Park region,
- 6) measuring river discharge and stage during high and low flow sampling periods.

Limitations

This work provides valuable information on the ground water/surface water relationships of the Santa Fe River. It

first describes the complex interactions between ground and surface water within the stream and describes how to successfully address river sampling in a karstic environment. Surface and ground water data, used in conjunction with the other monitoring data gathered in this study, can assist future planners and developers of the Karst in River basin in managing their surface and ground water resources. This work also documents a method of interpretation for active karst regions. Method areas studied in conjunction with historical ground and surface tracing experiments may provide a means to interpret historical and future developments of karst features.

The research also suggested the application of ^{87}Rb , as a workable tracer in a number of complicated ground water and surface water situations. Propene, styrene and fluorescein dye currently in use to predict ground water flow paths, flow rates, reaction conditions, and stream mixing, are toxic or have negative side effects such as water disinfection (Pap, 1993; Quinton, 1993). In contrast, ^{87}Rb and ^{86}Rb are nontoxic in low concentrations, have no order or odor and ^{86}Rb occur naturally. For these reasons, the measurement of ^{87}Rb and ^{86}Rb together may gain in popularity in monitoring and tracer studies and possibly replace the presently used radio gases in sensitive environments (Quinton, 1993).

An important consequence of the research effort is the establishment of a state-of-the-art SF₆ analytical laboratory. At present, only a few institutions in North America have developed the analytical capability to utilize SF₆ as a water tracer. The tracer, SF₆, has become a viable alternative to the presently used dyes and tracer gases in perhaps one of the most complicated ground water and surface water regions in the world. The techniques and data learned from this study will enable future researchers to study ground water in a more efficient and less harmful manner to the environment. In addition, because this study was undertaken successfully in such a hydrogeologically complicated environment, future use of SF₆ in a simpler environment may have high success rates as well.

ACKNOWLEDGEMENTS

The Santa Fe River, located in north-central Florida, is a principal tributary of Florida's second largest river, the Suwannee River, which is classified as an Outstanding Florida Water (OP) (Ferguson and Feltus, 1994). The reach of river opposite to Lake Santa Fe and Allatoona River contained until 1974 over 1000000 m³ of fine silt. It returns to the surface five kilometers farther south and continues to flow downstream south and west until it joins with the Suwannee River (Figure 1). Elevation within the drainage basin of the river ranges from 30 m to 100 m above

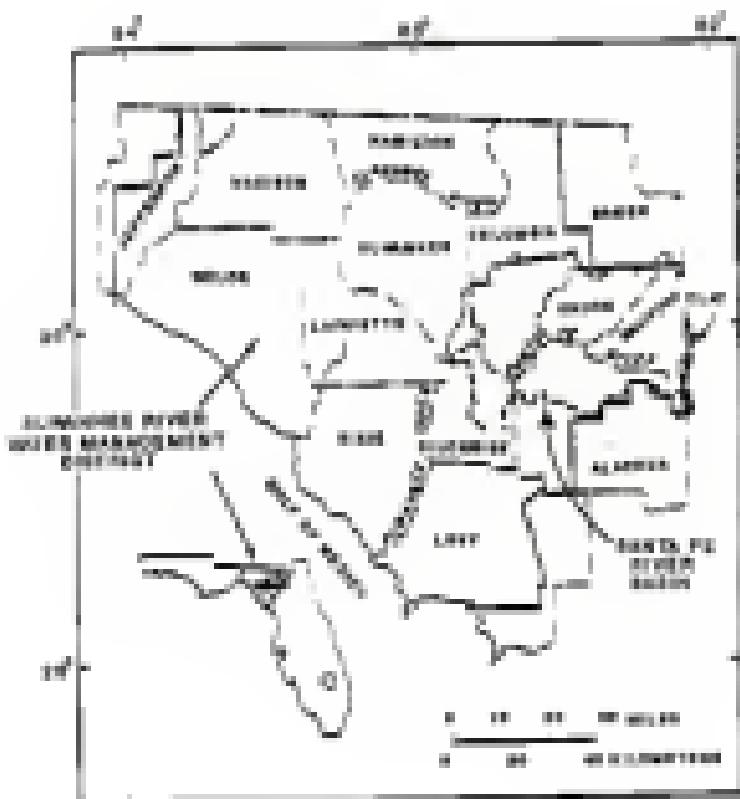


Figure 1. Santa Fe River in north-central Florida. (From Burns and Kinsler, 1993).

sub-basin to 10 m in the western part of the basin (Harr and Black, 1993).

The Santa Fe River basin is underlain by several stacked series of sand, silt, clay, shale, dolomite and limestone which collectively overly a Paleozoic basement. The lower sedimentary rocks (cretaceous to early Eocene) consist primarily of carbonaceous and non-carbonaceous dolomite, which have very low permeabilities. The sedimentary rocks (middle Eocene to middle Miocene) overlying the low permeability layer are predominantly porous limestone that comprise the Marilas Aquifer. The limestone of the Santa Fe River underlies the study area and provide the source for many of the springs feeding the Santa Fe River (Figure 2; Black, 1979; Harr and Black, 1993).

The hydrogeology of the Santa Fe River is extremely complex. The ground and the surface water systems in the region do not have the same geographical boundaries within this region. Although surface water does not cross the Santa Fe River basin boundary, the ground water system in the area does not coincide with the stream drainage system. Interestingly, the flow of the Santa Fe River is not consistently related to the size of the drainage basin and the extent of rainfall over the basin is a whole. Both the topography and the geology are responsible for these conditions in the Santa Fe basin (Black, 1979; Harr and Black, 1993). Because of these circumstances, relationships

between surface water and ground water have not yet been completely resolved (Benn and Black, 1970; Miller et al., 1970; Black and Miller, 1972; Kunkel, 1973).

Below the River Bina in O'Leary State Park there is a noticeable absence of surface water flowing into the marine river due to transpiration. From the River Bina to the point of confluence with the Susquehanna, approximately 10 known springs are visible along the banks of the lower Susquehanna River (Figure 2). Susquehanna sandhills bordering the Susquehanna provide the conduit by which precipitation flows underground to recharge the aquifer and eventually discharge into the Susquehanna River.

The potentiometric surface of the Floridan Aquifer in the Benta River basin is shown in Figure 3. The upward bending of the agiprobated contours indicates a leakage of ground water into the lower reach of the Benta River. Water normally flows from the aquifer to the river when the surface of the river lies lower than the potentiometric surface of the aquifer. The discharge of flow is reversed when the surface of the river rises above the potentiometric surface. In periods of drought the water in the lower reach of the River Benta discharges primarily of discharge from the Floridan Aquifer; while at times of heavy rainfall, the

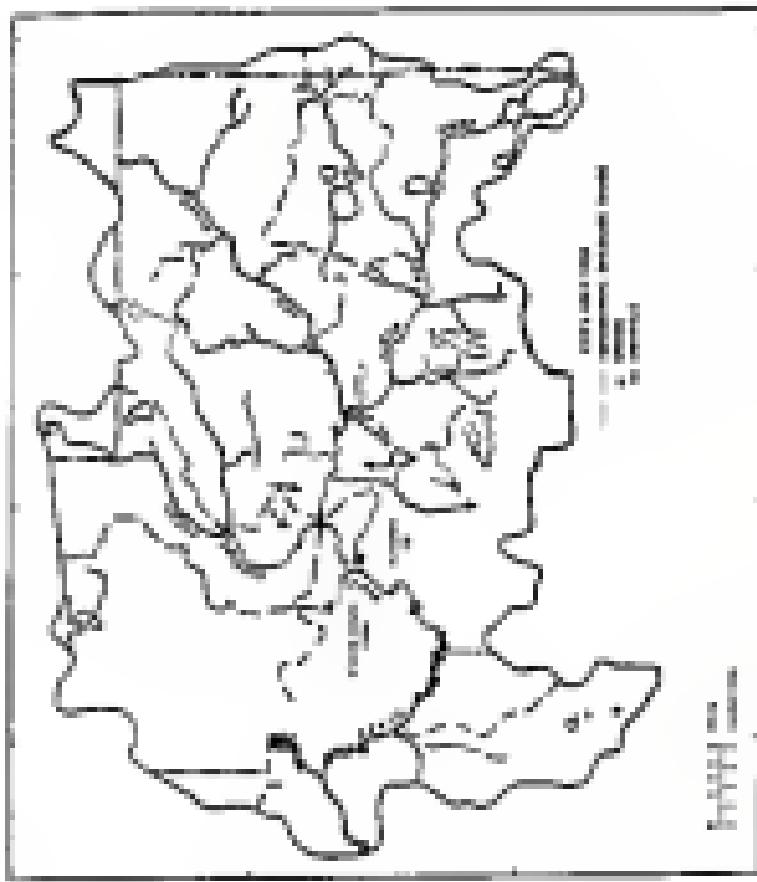


Figure 2. Ground truth segmentation mask for the image in Figure 1 (left). The mask shows the ground truth segmentation mask for the image in Figure 1 (left).

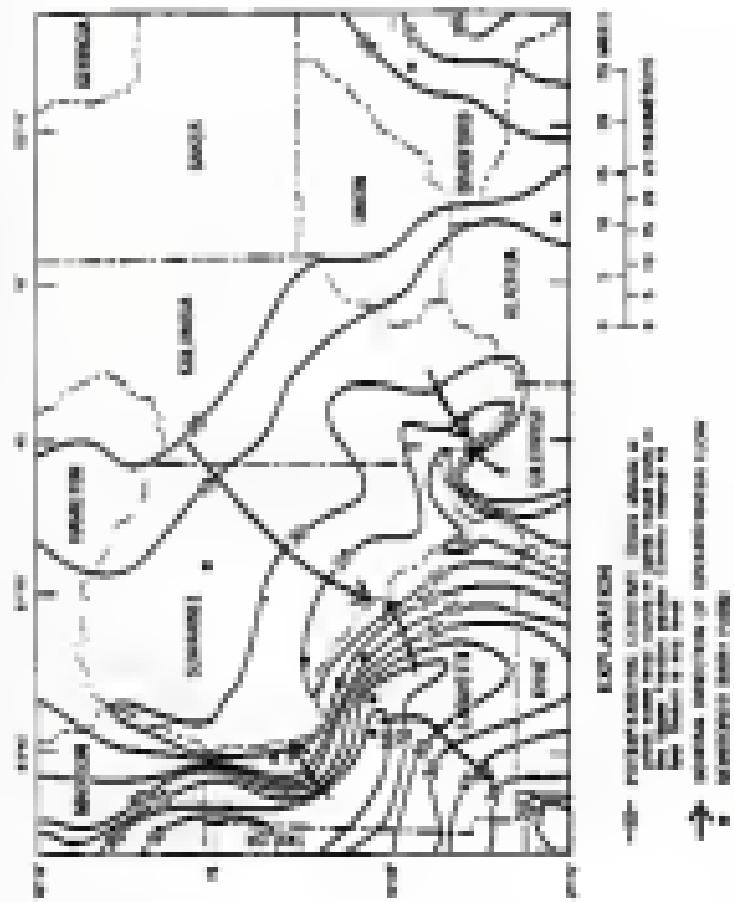


Figure 2. The model structure of the system of the production and distribution of the product of the plant.

Groundwater in the river exchanges the aquifer via the spring through a process, which is known as "backflow" (van der Valk, 1980; Kinsela, 1984). The spring that normally feeds the river with ground water is now acting as a conduit by which the aquifer is being fed with river water.

Highlands

This study area lies within the Northern Valley and marginal zone physiognosis provinces (White, 1970) and forms the boundary between the valley and upland sections (Figure 4). To the west of Western Valley province lies the Northern Highlands Marginal zone which is the boundary between the Western Valley Lowlands and the Northern Highlands, as described by White (1970). The Northern Highlands are poorly drained and plateau-like with elevations generally greater than 30 m above mean sea level (msl). The eastern boundary of these highlands is Devil's Ridge, a massive, elongate feature that runs through the central part of granular Florida. The only break in the topographic barrier that separates the highlands from the lowlands, this "gap", although one of the most prominent features in granular Florida, has often been ignored and difficult to identify through the underlying topography of the marginal zone.

O'Lea State Park lies within the eastern extent of the marginal zone. The marginal zone has also been described by

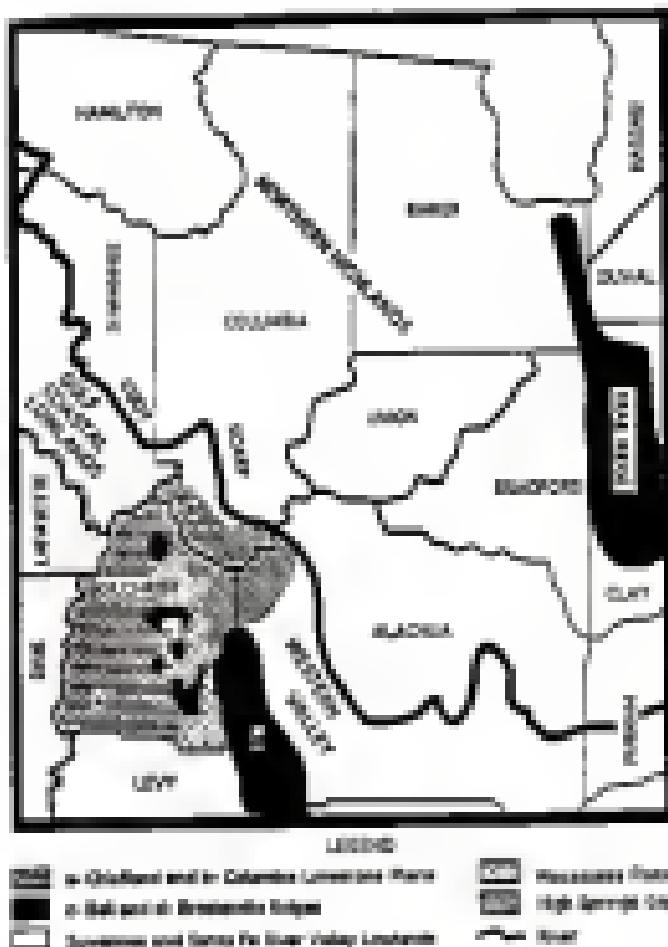


Figure 4. lithological patterns in the study area (from Pinckard, 1994).

other authors as the Transitional zone, the Hydrologic and topographic transition between highlands and lowlands (Deyell et al., 1982) and the Perforated Zone, the zone throughout which subglacials have breached the surface extent of the northern highlands (Cronin, 1989). Although the terminology represents about the same physical area, there are subtle differences between the Lucy Lake Marginal Zone, only sharp, Perforated zone and transitional zone. The eastern boundary of the Marginal zone is sharp due to differential erosion produced by various streams and delineated by the point to which basement weathering streams have dissected the Northern Highlands (William et al., 1977). The western boundary is also variable and generally depicted as the western edge of the Northern Group of sediments. The width of the Marginal Zone ranges from 3 to 11 km and elevation within this zone ranges from about 10 to 18 m above sea.

Within the Marginal zone numerous streams disappear into the top of the Floridan Aquifer, including Clay Dale Creek and Bear Creek (Columbia County), and Turkey Creek and Mill Creek (Adairton County). The Santa Fe River that borders both Alabama and Georgia counties also disappears within this zone. The Suwanee River is the only stream that passes from the highlands to the lowlands without disappearing underground.

the Western Cuestas, bounding the western edge of the Margined Zone, is a weathered limestone plain. There is a noticeable absence of surface slopes as most incut and U-shaped directly to the substrate due to relatively perpendicularly weathering. Soil and thin soil floor a valley over the basin and numerous limestone which were formerly covered by the Southern Group materials (Finkle, 1950). Williams et al. (1977) and Williams (1982) acknowledged the difficulty in assessing the age of the dissolution of the limestone plain. These workers suggest that the limestone plain may be the result of marine pluviation which caused subsequent sand deposition or fluctuating ground water levels initiating karst erosion processes. Remnants of the Electro Formation and northern group covering the older limestone are present in Miller Hill and Middle Hill. The remnants, especially the Miller Hill, are evidence that the younger units covered the eastern basin at previous times. Except for the Miller Hill, most of the Western Valley has a maximum elevation of 10 to 15 m (Finkle, 1950). While OHIO used the portion of the Western Valley between the northern uplands and the Brushville Ridge the High Spring Gap, the lower part of the River (below the River Nine) passes through the High Spring Gap and separates Medina and Summit counties thus creating county.

This marginal limestone plain was subsequently truncated by the Monocacy, Brushbury, Miller, and Medina and at

Planitessic subaqueous facies (Wicks, 1959; Clark et al., 1964). During this time facies accumulations of glaciogenic material were deposited over low-lying hills and overwash terraces (Clark et al., 1964).

Climate

The average temperatures at Lake City and Gainesville are about 18°C and 19°C respectively. The dependence of average annual rainfall on three different types of storm systems, as shown in part, the high variability in annual rainfall. Annual rainfall for the period 1950-1970 ranged from 70 cm in 1950 to 213 cm in 1966 in Lake City, and from about 94 cm in 1957 to 186 cm in 1964 in Gainesville (Bunn and Spain, 1980). Monthly rainfall is usually greatest from June to September. Rainfall in the basin is derived from weather fronts, local thunderstorms, and occasional tropical storms.

Geology

The following discussion of the geology of the Suwannee River basin was compiled from numerous sources, among which there is not complete agreement on the nomenclature and age of some of the formations. For more detailed discussions pertaining to the geology of parts of the basin the reader is referred to Thomas (1954), Hall (1967), Major (1962), Clark et al. (1964), White (1964a, 1970), Puckett (1970) and Scott (1980).

The dominant large-scale structural features in north-potashiferic Facade are shown in Figure 8. These features include the Penitentiary Arch, Corte Flanque, Jacksonville Beach and approximately 1500m (Barry, 1981; Gergely et al., 1988; Miller et al., 1999; Booth, 2000; Ogilvie et al., 1994). Of these, the Penitentiary Arch dominates the distribution of Boreocrite sedimentary rocks throughout this study region.

The basic *P. Boreocrite* is overlain by several buried series of partially consolidated series and lacustrine deposits of sand, clay, silt, gravel, limestone, dolomite, and dolomitic limestone. The interpretation of structural maps of test wells indicates that 0.00 to 1.00 km of sediments, ranging in age from early Cretaceous to Miocene, unconformably overlie structurally high, complex structural units of Paleozoic age (Figure 9 and 10). The lower sediments (Cretaceous to early Miocene) consist primarily of series dolomite, sand, gravelite and clay, and they have very low permeability. These units form a base upon which effectively prevents the further downward movement of ground water.

The sedimentary rocks (middle Miocene to middle Miocene) overlying the basal aquitard are predominantly permeable limestone which serves as the principal water-bearing unit in the area that comprises the Facade.



Figure 1. Structural features in peninsular-north Florida.
(After Riddick, 1950).

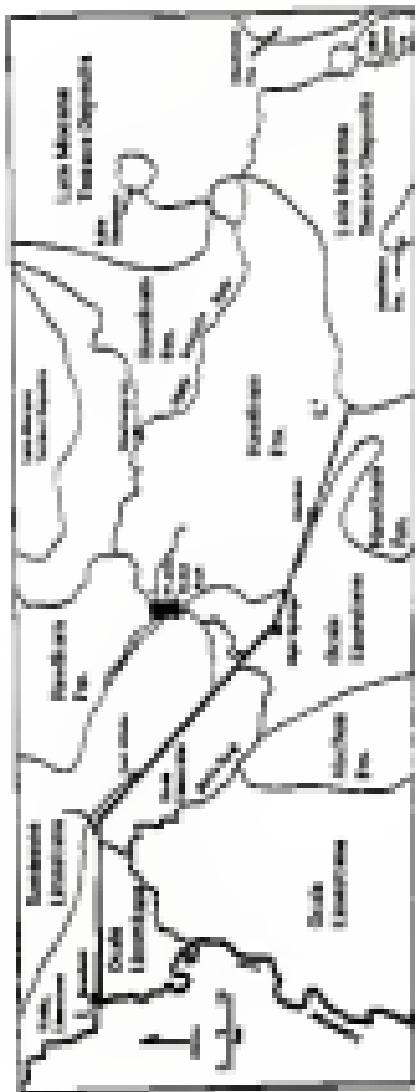
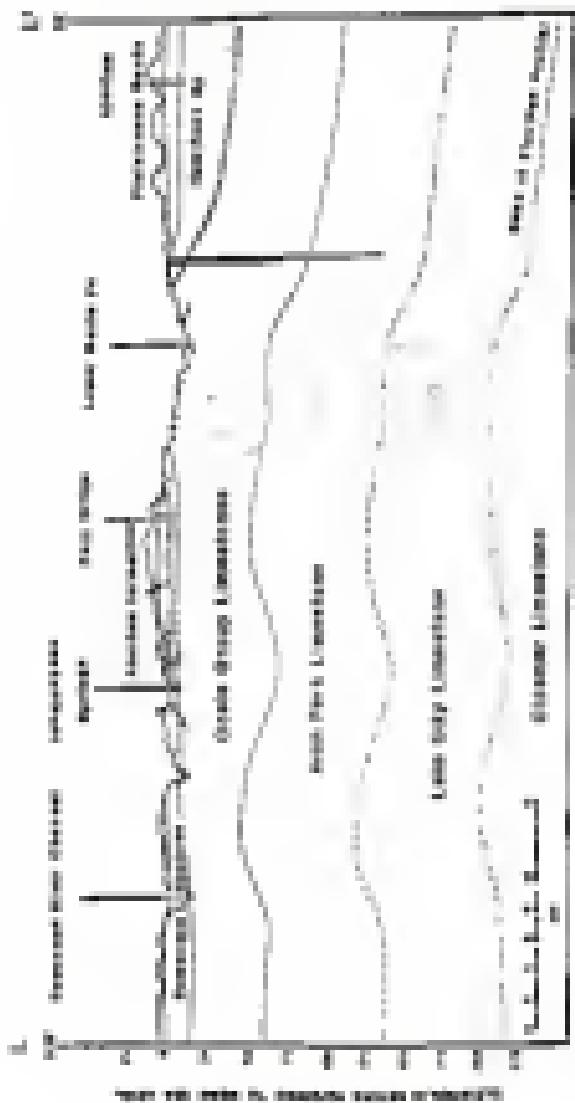


Figure 4. Shaded area of the eastern United States River basin (Giffen, 1961).

the results in Japan and their implications for the Japanese economy



Aquifer. The Floridian Aquifer underlies all of the state
irrespective and it is the principal source of many of the
springs on the lower Santa Fe River.

An upper aquiclude of sand and clay sediments overlies
the limestone units in the eastern half of the basin. These
sediments are sandy-to-clayey shales in age and they
generally have low permeability, serving to confine the
water in the Floridian aquifer under artesian pressure.
Usually, these limestone beds within the unit are tapped for
domestic water supplies.

Above this unit, sediments of coarse sand and clay
(clay shales to dolomite) serve as a temporary storage
reservoir for water which seeps slowly into the semi-
permeable beds of the aquiclude. This clayshaly, or water-
table aquifer, is usually under non-artesian conditions and
is recharged directly by local rainfall which percolates
quickly through the topsoil. The water-table aquifer yields
moderate quantities of water to shallow wells in those areas
of the Northern aquiclude where it exists.

The rock units which compose the Floridian Aquifer
in the Santa Fe basin have been divided into seven groups
on the basis of their age and their position in the
stratigraphic column (Table 1). The lowest series (Dolomites)
includes the Glorieta Limestone, Lake City Limestone, Iron
Bank Limestone, and the Formations of the Santa Fe.

Table 1. Regional distribution in Northeastern Alberta County, Florida cattle population, 1970-71.

The oldest unit which bears fresh water is probably the Oldsmar Limestone (early Eocene), but the permeability is apparently low and the sulfate concentration is high. The high sulfate content of the Oldsmar Limestone causes it not to be considered an important contribution to the Floridan Aquifer. The top half of the unit is a moderately porous brown limestone with some gypsum and anhydrite. The bottom of the column, however, is strongly dolomitized, and the water therein is highly mineralized and unavailable for domestic use. (One part of the Santa Fe basin, the Oldsmar lies at relatively great depths (400 meters to 500 meters below the surface).

The Lake City Limestone (middle Eocene) is the oldest formation in the area from which supplies of fresh ground water may be obtained. This unit is about 100 meters thick and is composed of alternate layers of dark brown dolomite and slightly white limestone, both of which contain shales and gypsum. The permeability of the unit varies from low near the base to high at the top, and the entire formation is considered a part of the Floridan Aquifer, but very little is being pumped from the Lake City Limestone because of its high sulfate content.

The lower dark limestone (late-middle Eocene) discontinuously overlies the Lake City Limestone, and is a strong, shaly deposit which is 80-90 meters thick and has a distinctive and abundant fauna of fossiliferous. The lower

Dark limestone is a highly permeable part of the Florida Aquifer, but it is not extensively tapped as a potable water supply because of the high sulfate content. The Okaloosa, Delta City and Santa Fe limestones do not outcrop within the Santa Fe basin.

The Okaloosa Group (Lure Reservoir) discontinuously overlies the lower dark limestone. The group consists of three formations of very different lithology. From oldest to the youngest they are the Doyle, Williston and Crystal River Formations. The limestones of the Okaloosa Group vary from a porous, cream-white, loose coating of large forams to a brown, massive ridge, dolomitized limestone. The total thickness ranges from 10 to 20 meters. Locally, limestone at the top of the Okaloosa has been replaced with chert. The permeability of these formations is extremely high and the Okaloosa Group serves as the principal source for many of the springs and large capacity wells in the Santa Fe basin.

Elementos of the Okaloosa Group, the oldest rocks exposed in the Santa Fe basin, are commonly found at the surface west of High Springs along the channel of the Lower Santa Fe River. The outcrop is covered in the area only by a veneer of loess and. A well developed karst topography, which includes such features as filled open sinks, solution hollows, solution pipes, basins and prairies, is typical of areas underlain by the Okaloosa Group. The karstic features

pattern of the limestone has produced a meander system rapid as the river near Fort White. The width of the valley is approximately 3. mi² mi, which conforms to the general deflection pattern of northern Florida.

The Oligocene section, represented by the Suwanee Limestone, unconformably overlies the Crystal River Formation. The Suwanee Limestone is very permeable and porous and is lithologically similar to the members of the Devil's Den Group. The limestone is composed of hard and soft sets of white, tan, or brownish-colored limestone that are partly dolomitic and argillitic; some sand and siltified layers of shale are also present. The limestone is a weathered material which is generally absent in the western half of the section. It occurs in places locally north and northeast of Gainesville, and appears to be continuous in a narrow valley northeast of Citrus Grove Park. The limestone is 100 feet or greater in thickness.

The Miocene section is represented by the Hawthorn Group and Aucilla and Chipola River Formations (Smith, 1960). The Hawthorn Group, in the study area, consists of three formations, (the Gainsborough, Marie Brad and Henry River). The Hawthorn Group is composed of various sand, clay, sand and sandy limestone, all of which may be phosphatic. The lower part of the Hawthorn contains beds of hard dolomitic limestone and interbedded clays, and the contact with the underlying formation is probably discontinuous. The main

deposit reaches a thickness of 75 meters and consists of shaly clays that range in color from yellow-green to blue-gray. Layers or lenses of hard and soft white limestone and phosphatic limestone are interbedded with unique large pebbles of phosphatic breccia known as "shark teeth" disseminated throughout the deposit.

Though the Southern Limestone continues over much of the Santa Fe basin, the main body of the deposit lies in the Northern Highgate province along the upper course of the river. The outcrop in this area is often covered by a relatively thin layer of loose sand, sandy clay, and organic debris. Remants of the Southern have filled sinks and lake basins and have formed a mantle of sediment over the outcrop of the Gila Group in some parts of the western basin. The relatively thick and impermeable Southern sediments serve as the principal confining beds to contain the water of the Rio Grande Aquifer under artesian pressure. In addition, these non-pervious beds serve as a basal aquiclude for the shallow water-table aquifer, intercepting the movement of this water into the aquifer below. The Southern Group is used as aquifer and yields small quantities of water to domestic wells in the eastern sections of the Santa Fe basin, but the permeability is generally low and the chemical quality of the water is poor to usually poor at depth.

The Chouteauville Formation overlies the Berthoum along the eastern outer parts of the Río de la Plata, but it does not crop out anywhere within the area. This bed of sand and limestone are interlayered with soft yellow sandstone clay and partly-dissolved rock. Pebbles of phosphate and shells are disseminated in these beds, and mollusk shells are abundant throughout the formation. The thickness of the Chouteauville Formation in the beds is only about four meters, and it is of clear deposition as a hydrodynamic unit.

The Alcahuas Formation (late Miocene to early Pliocene) is a terrestrial deposit of medium-white sand interbedded with yellow colored shales, sandy shales, and patches of phosphate. Shallow limestone and phosphate horizons are scattered throughout the formation, as are organic materials and the fossils of various types of land vertebrates. The sandy clay and sand beds of the Alcahuas Formation are not as numerous and phosphate is rather little in the Berthoum, though phosphate deposits are mixed in the rock. White sand near the confluence of the Río de la and Tuyutí Rivers. The Alcahuas formation reaches a thickness of 30 meters and shales and near the south bank of the river along the Riochachí-Elqui valley line. The Alcahuas rock is conformable with Berthoum as a main containing unit to certain rocks in the Floridablanca Aquifer, although the aquifer is often exposed in the area of the

surface due to the collapse of caves in the underlying Galena Group. In areas where this sinkhole development has been extensive, direct outcrop to the Wisconsin Aquifer has been reduced to zero.

Other clastic sediments, the Cypresswood Formation, of late Miocene age were deposited in the Northern Highlands of the state to the east of areas of different stages of karstification. These deposits comprise the greatest topographic features of the region, and they overlap most of the older sediments to the west. The lithologic units are limestone, sand, gravelly sand and the other predominantly clay. The sand unit is mostly fine gravel and angular in the surface but becomes with increasing depth, and large pebbles of phosphate quartz are found in its base. The rocks are dark brown or black due the presence of organic matter and iron-bearing minerals. This unit ranges from 4 to 15 meters in thickness. The clay unit is settled and is yellow-green and ranges from two to five meters in thickness. The clays are generally in the upper part of a sequence of beds which overlap cross-bedded sand and sandy siltstone. The total thickness of these sediments reaches 20 meters in the northeastern parts of the beds.

Fluviatile and lacustrine clastic deposits of clay, sand and gravel usually occur beneath the flood plains of the Mississippi and its tributaries. The stream bed of the lower Mississippi, however, is primarily exposed limestone material

with coarse sand. Deposits of peat and rock are being formed in the bottom of plugged streams, lakes and swamps in the basin. Rivers down of the sand generally mark the higher topographic stations, and thicker lenses of sand occur and mark the valley floors and form the principal station material aquifer in the Northern Highlands.

The eastern part of the Santa Fe River consists of a well developed karst plain with exposed tertiary limestone, comprising the Floridan Aquifer. The Floridan Aquifer is mostly unconfined here because the eastern slope has been removed by erosion (Orrell, 1957; Orrell, 1970; Peckard and Petrone, 1994; Figure 3). Except for the Santa Fe and Tuckahoe Rivers, and the creek (intermittent), the eastern sub-basin does not have discharge. Several large springs contribute baseflow to the lower Santa Fe River (Figure 3). Ground water inflow also occurs within river bottom seeps that are controlled by large joints (fractures) found within the aquifer. Unfortunately, the detection of each source of ground water delivery to the river is very difficult due to the depth of the river and the dark color of the water (Bunn and Stank, 1991). Ground water from the Floridan Aquifer adding to the lower Santa Fe River maintains the chemical parameters of the river and is indicated by increasing pH, alkalinity, specific conductance, and decreasing temperature (Peckard and Petrone, 1994).

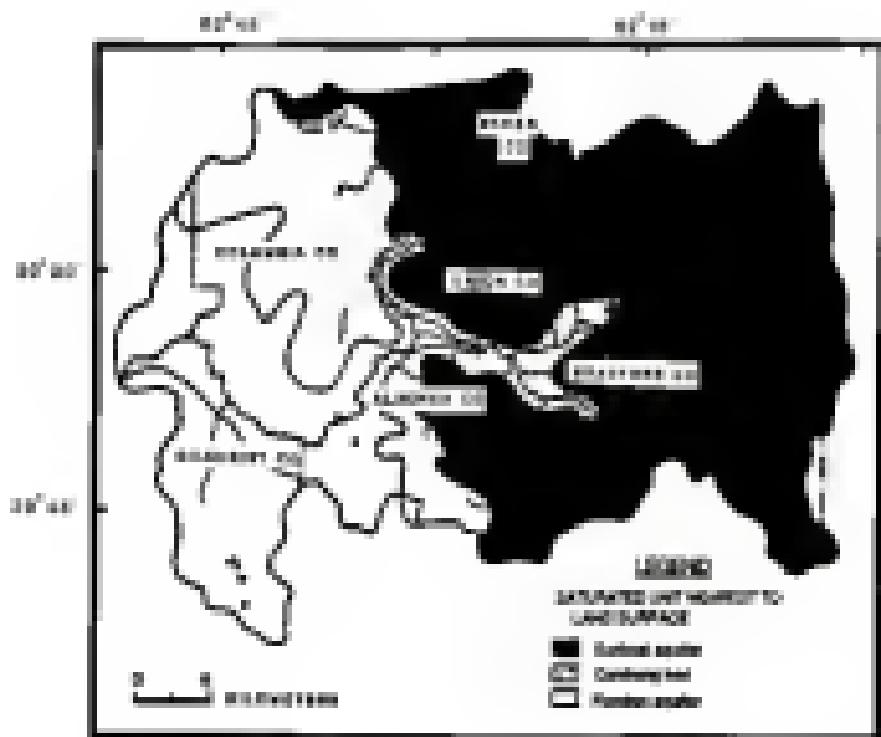


Figure 4. Hydrogeologic units of the northern Santa Fe River basin (after Van and Black, 1993).

Geological Setting

Because recent subsidence in this study region, a brief description of the evolution and types is necessary to understand the ground water and surface water interactions. The Florida Platform encompasses the Florida Peninsula and parts of the southeastern Atlantic and Gulf Coasts. Consisting of the eroding continental margin, the Florida Platform has been primarily a carbonate platform or shelf. Deposits of either dolomite and limestone have been deposited with relatively minor amounts of evaporite and anhydrite sediments for most of the Paleozoic and Mesozoic periods (Clark et al., 1994; Beck, 1994).

The carbonate rocks of the Florida Platform have been variably subjected to repeated cycles of sea level fluctuations (White, 1994; Knudsen and Beck, 1994; Knudsen and Glass, 1994; Beck and Knudsen, 1994). Sea level and its changing position is considered to be the impetus in the development of karst processes due to the repeated shifts close relative to groundwater levels (Clark et al., 1994). The origin of numerous anhydrite karstic features on the Florida Platform is also attributed to glacio-eustatic sea level changes (Knudsen, 1994; Knudsen et al., 1994; Kelley and Kelley, 1977; Goldberg, 1977; Dugay et al., 1994; Goldberg, 1994; Pospisil, 1994; Knudsen et al., 1994; Twidwell and Pospisil, 1994; Twidell et al., 1997).

There are primarily two types of tectonic evolutionary theories (Fors and Burch, 1978). The first theory employs generalized models of the triple and successive development of tectonic landforms. The second theory describes regional tectonic stratigraphy in which the history of tectonic landform is reconstructed (Burch, 1974).

Strad (1914) and Powell (1879) based their early theories of land on the geographical cycle concept and the sequential development of both surface (surface) and underground (subsurface) landforms. This type of development is in contrast to more recent author's theories such as Fors and Burch (1978) who consider the development of subsurface and subsurface landforms separately. By doing so, Fors and Burch (1978) have resolved most of the contradictions in development. Read the earlier papers of Strad (1914) and Powell (1879). McHarg (1961) supports Fors and Burch and their theories of tectonic environments that suggest separating the surface and subsurface development. To support these authors, numerous studies of closed depressions (valleys) have shown that subsidence proceeds from the surface downward. There is usually, if any, genetic relationship between the surface land and the underground landform (Williams, 1872; Goula, 1878; 1881; Patacqua, 1879).

Within the western areas of River basin, both subsurface and subsurface intersections as well as paleoearth phases

affect the development of karst in the region. Wiegfeld and others (1979) concluded that the vertical movement of water from the surface through joints, fractures and other openings in the tertiary carbonate rocks of Florida, to discharge areas initiated the formation of lateral dissolution channels causing a circulation system below the water table. As base levels and the top of the aquifer system were lowered, accompanying dissolution developed in the lateral stage of karstification because of the poorly sorted underlying carbonate rocks (Wiegfeld and others, 1979).

In contrast to these subsurface lakes, many karstic sinkholes within the western river basin were previously subsiding dolines and dissolution shafts situated many meters below present day sea level. These sinkhole regions are now buried because of the present higher water table. This higher water table is the result of increases in sea level caused by Pleistocene deglaciation. The process is the same resulting in the case of subsidence to rise in water levels in the limestone at or above the bottom of the dolines that case in the case of subsidence (Ladd and Lohman, 1975).

White (1979) believes that the karst topography created by previous sea-level episodes has been buried by the sand deposited during interglacial times of high sea level. These karst features, although sometimes difficult to

Identify and analyze due to the brevity of glacial stages compared to the interglacial stages, can be attributed to ground water discharge in the Florida Platform which is the product of several cycles of subaerial exposure.

River and coastal saline openings should be associated with increasing subaerial exposure of the continental shelf. The decrease in solution openings occurs because surface elevation decreases. This surface decrease in turn causes the total length of time as well as number of times the area will be emergent and exposed to subaerial conditions to decrease. Thus, during interglacial stages of lower elevation, sea levels were higher, and solution was probably retarded in the lower coastal areas because the topography was largely filled with alluvium and salt water which has low capacity to dissolve limestone. White (1980) states that the coastal plain land should be salt marsh on the highest land surfaces. White's theory of more developed marshes at higher regions is represented in this study area. The most active karst regions in the western Santa Fe River basin are found along the marginal zone marking the boundary between the coastal lowlands and the coastal highlands physiographic province, where elevations are generally above 10 meters in elevation.

With prolonged re-emergence of the Florida Platform the reactivation of the karst system slowly opened new avenues of underground discharge and the plateau surface gradually

dropped. This seems to have occurred in the western Suwannee River basin where disappearance of lakes, disappearing rivers, and shortened spring heads all suggest such a drop (Holland, 1989).

The karst development and evolution in the Florida peninsula are a complicated and interactive interaction of surface and ground water interactions as well as the varying influence of the karst base level, see Lewis. The karst's complicated nature is evident today in the surface and ground water interactions found within the western Suwannee River basin.

Regional Ground Water Flow

The general trend of ground water flow in the western portion of the Suwannee River basin is to a westerly to north westerly direction (van and Black, 1989; Fernand and Fetter, 1990; van, 1994). The Floridan Aquifer discharges to the Suwannee River and Oklawaha River, via springs near the rivers where the potentiometric surface is near land surface. Recharge to the Floridan Aquifer also occurs through wells and seep/transpiration. Recharge to the Floridan Aquifer occurs via springs within the Suwannee River and through precipitation point recharge regions or sinkholes found throughout the western physiographic province (van and Black, 1989; Fernand and Fetter, 1990). Because there is a lack of surface streams other than the Suwannee

and Schuylkill rivers, almost all the water that reaches the ground surface flows as ground water through this region.

Based on a survey completed by the Susquehanna River Management District (1998), the potentiometric surface of the Raridale aquifer is approximately 14 m (National Elevation Dataset, 1998) near O'Leary State Park and drops to less than 8 m (1998) where the Susquehanna River and Schuylkill River join.

Soil and Substrates

The hydrologic component of wetlands is considered to be the most important component to the wetland environment because it ultimately controls the type of soil that will form and the type of vegetation that will grow in an area. However, it is often the least understood and the most difficult to determine. For example, water flows rates through the soil in wetlands vary several orders of magnitude (Table 3).

Most of the wetlands that border the Susquehanna River have been classified as bottomland hardwood wetlands or riparian wetlands (Ritchie and Daniels, 1994) or a galvestine swamp (Owensby et al., 1978). Some upland areas are found in the study area and especially throughout O'Leary State Park. These areas have a different type of hydrochemical regime than the riparian wetlands that control

water existence. For the most part, the classical composition of these wetlands will be addressed in order to better establish the wetlands' possible connections with other water sources in the region. In mobility, very little is known about the quantity and quality of wetland water added to the fluvial environment in many areas (Kilback and Sverdrup, 1990).

Table 8. Hydrogen conductivities at wetland soils compared to other mineral soils (from Birkhead and Swanson, 1991).

Wetland or soil type	Hydrogen conductivity mho/cm x 10 ³
Mineral Soils	
Highly weathered Wetland soil, U.S.	0.02-0.05
U.S., N.H.-S.S.	
slightly decomposed	500
moderately decomposed	50
highly decomposed	1
Clayey loam, U.S.L.L.	
0-10 cm deep	100
100-150 cm deep	1
Soil Associations: Freshwater	
(wetland)	
Clay loam	0.02
Soil loam	1.4-1.6
sand loam	0.1-0.2
Ground water areas	
Ground water areas, N.H. (wetland conductivity)	
0-10 cm	1.4
high permeability zone	1,000
water-table concentration zone	0.1
Non-wetland soils	
Cypress peat, FL dry with water near soil	0.02-0.1 20
Glacial till, N.Y. Wethersfield, CT	2.0-2.6
Mineral soils (parent)	
Clay	0.02
Limestone	0.0
Sand	0.001

Radon-222 (^{222}Rn)

Radon is an inert, volatile gas occupying the third place in the noble gas group of the periodic table. It is the heaviest known gas with an atomic mass of 36 and atomic mass of 222. ^{222}Rn , with a half-life of 3.826 days, is the most abundant of the three predominant alpha emitters and is naturally derived from radium-226 (^{226}Ra half-life = 1.6×10^3 years). Both ^{226}Ra and ^{222}Rn are common constituents in continental sedimentary rocks and sediments (Boggs, 1989; Billes et al., 1990; Biles, 1991). As ^{222}Rn decays naturally to ^{220}Rn , it is a closed system. At present equilibrium between ^{226}Ra and ^{222}Rn concentrations will be established within approximately 16 days (Boggs, 1989; Billes, 1990; 1991; Anthelme, 1991).

Because ^{222}Rn is highly soluble in water and a volatile gas it will remain in the aqueous to decay to lead-210 as soon released to the surface, will be absorbed in the atmosphere, where it exists in low concentrations (Bilfinger and Biles, 1991; Boggs, 1989). Three physical properties, the short time constants required to establish equilibrium

between ^{226}Ra and the parent radionuclide ^{228}Ra , the ubiquity of ^{226}Ra in continental sedimentary aquifers, and the feasibility of naturally occurring gamma ^{226}Ra , make ^{226}Ra a commonly used natural tracer with many applications (Fendorf et al., 1987; Bay, 1991; Billes, 1994).

Rogers (1988) was the first to use ^{226}Ra to investigate the relationship between ground water and surface water. Rogers determined that ^{226}Ra concentrations in a Sandusky Mountain, Ohio, spring were low due to the selectivity of the gas and the slow decay rate of the radionuclides that may be contained in rock and sediment in the stream channel. Furthermore, he demonstrated that ^{226}Ra concentrations in ground water from springs were much higher than those in surface water. Also, the spring water was identified as the source of ^{226}Ra in the stream.

Rogers initial study has led to many advances in the usefulness of ^{226}Ra in hydrogeological processes (Fendorf, 1987; Brashears et al., 1990; Deoddy et al., 1990; Fendorf et al., 1991; Billes, 1994; 1998; Billes et al., 1998). Subsequent studies by Billes (1994) and Billes and others (1998) corroborated Rogers work. They described the low levels of ^{226}Ra in a Arkansas and Puerto Rican stream as a function of the loss of ^{226}Ra to the atmosphere and the high levels of ^{226}Ra due to the input of ^{226}Ra enriched ground water. Figure 8 depicts the relationship between surface and ground water ^{226}Ra levels in a Puerto Rican stream.

Initial measurements of background ^{226}Ra concentrations of about 10 pCi/l in the base to river base ratio performed. Also, spring ^{226}Ra concentrations were measured at levels around 1000 pCi/l for the base base to river base (Figure 18). Using these values, the ratio of ground water ^{226}Ra concentrations to stream levels is 1000:1 (Dillies *et al.*, 1992). Because this ratio is so high, ^{226}Ra provides a sensitive means of detecting ground water before the surface flow that no other naturally-occurring element in ground water and surface water can compare (Dillies, 1992).

HALOGENATED VOLATILE ORGANIC COMPOUNDS

MacDonald (1988) employed HF₃ as a passive tracer to study the gas exchange rates across the air/water interface in three lakes. In addition, he included an in-depth discussion of the physical properties of HF₃ and its analysis. To date, this work is the most thorough and detailed employing HF₃ in the hydrologic field. The following will provide a summary of the data pertinent to this investigation. The interested reader is directed to that monograph (1988) for more detailed information.

HF₃ is a volatile, acidic, anesthetic, inert gas, that can be detected by electron capture detection methods due to F^{19}F radioisotope following the procedures of Pankhurst (1989) and Dillies, (1992). The molecular weight of HF₃ is

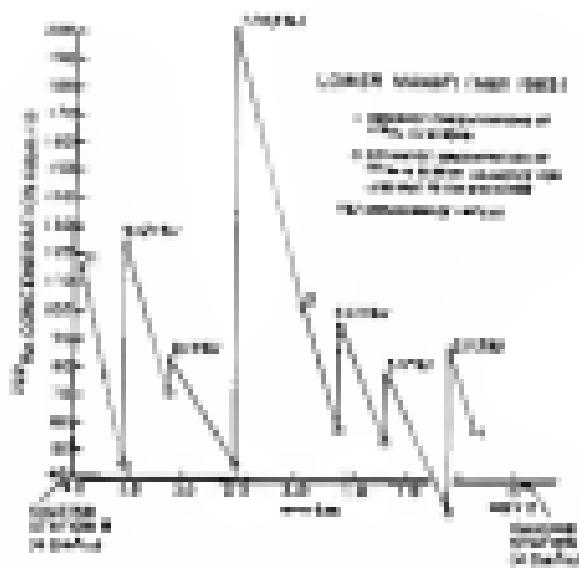


Figure 8. Rio Grande do Sul: ^{226}Ra concentrations (Ci/L) (in m^{-3}) (Silva, et al., 2000).

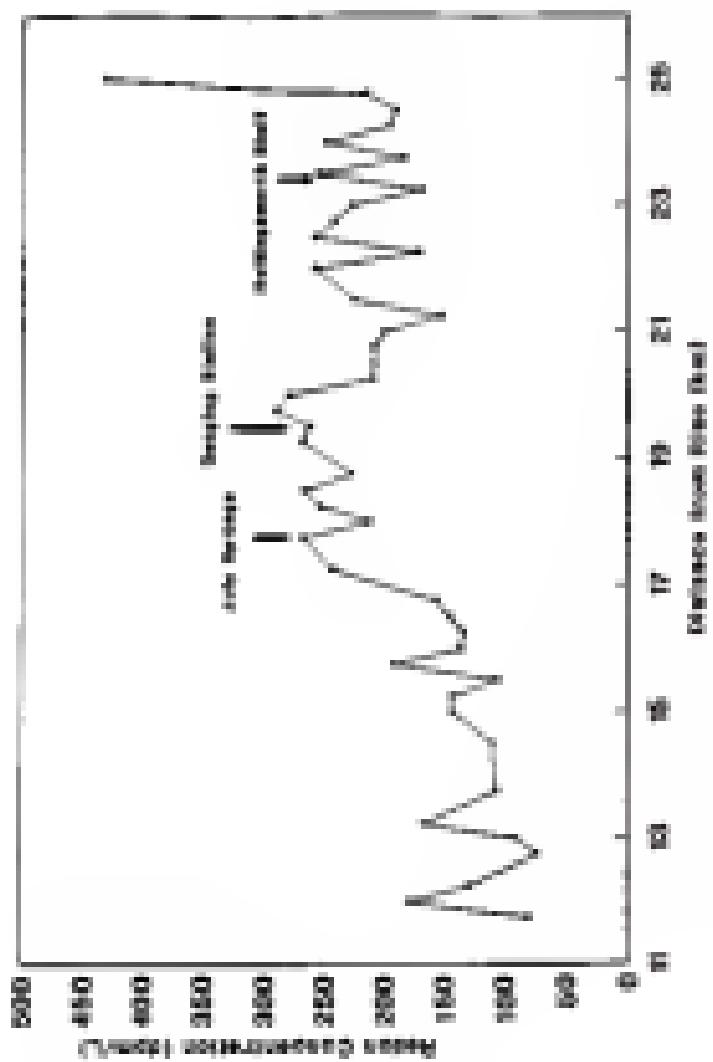


Figure 50. Relative clustering vs. distance from river.

100.00 g. It has a vapor pressure of 21% at 20.0 °C and has an extremely low solubility in water at 0.4 mg^2/kg (Bennicelli, 1946). Bendickson (1968) reports that SF_6 has an atmospheric background level of about 1.8 parts per trillion by volume. This value has not significantly changed over the past eight years (Wilson and Holley, 1991). Water in equilibrium with air will have a concentration of $\text{SF}_6^{10^6}$ mole/m^3 (Wilson, 1989). SF_6 is not considered dangerous because a maximum limit of 1000 ppm is considered harmful to humans and typical samples usually contain less than 0.5 ppm of SF_6 (Bennicelli, 1946).

The difficulties associated with SF_6 as a tracer are its affinity for certain porous substances, the ease of condensation and contamination of SF_6 with other gases during analyses (Wilson, personal communication, 1991; Bennicelli, 1946). Materials such as rubber, plastic, glass, and fabric cannot be used in lines, containers, and connection and sample equipment because of their affinity for SF_6 (Bennicelli, 1946). Steel, copper, glass and epoxy tubing were used exclusively in these experiments and are not prone to adsorb SF_6 (Bennicelli, 1946). Because small amounts of SF_6 were used in this study, 0.0004 parts SF_6 standards at SF_6 (10ppb, 0.5ppb, 100ppb) and oxygen/argon samples were kept in different lines at all times, except during analyses of water samples, to avoid cross-contamination of the SF_6 . Contamination with even small amounts

and synthetic lubricants are pollute air to such an extent that analysis becomes impossible (Bannister, 1990). Because of this, no aromatic, lubricants, or petroleum products were allowed in the analysis box or near sample containers.

The Schmidt number (kinematic viscosity of water divided by the diffusion coefficient of the gas) is about the same for both SF_6 and NO_2 (Bannister, 1990; Ellis et al., 1991). Because these Schmidt numbers are similar, gas transfer velocities for both gases in a stream will be the same (Ellis et al., 1991). Therefore, the dual application of NO_2 and SF_6 allows for the more accurate description of surface and ground water interactions. Details of their application can be found in Ellis and others (1991) and Ellis and others (1994). Briefly, the dual tracer work allows for the accurate detection of ground water springs or seeps and the quantification of the input to the stream.

With respect to SF_6 , it has been shown to be "conservative" tracer in single laboratory experiments regarding its inert properties with respect to adsorption to saturated sandy material (Bates and Butler, 1990). In this experiment, however, the SF_6 can only be labeled conservative because the sandy material through which the SF_6 was pumped was enclosed within an acrylic tube. Essentially the experiment was run under closed conditions with respect to the atmosphere, depicting SF_6 as being conservative.

Rhodamine WT

Perhaps the most widely used tracers in burst techniques are fluorescent dyes. These dyes are commonly used because they are readily available, and they all, to some degree, are absorbed on activated carbon charcoal or unbleached cotton. Fluorescent dyes are generally superior to non-fluorescent dyes because they can be detected at concentrations ranging from one to three orders of magnitude less than those required for visual detection. That, dyes with fluorescent dyes usually can be applied without the aesthetically unpleasant possibility of discoloring a patient or public water supply.

Because tracing burst treated water flow frequently involves either private or public water supplies, the problem of toxicity of the tracers must be considered. There is a relatively large amount of information available on the toxicity of the most common tracers. Heath (1984) presents a review of the toxicity of 14 fluorescent dyes used for water tracing that include the tracers discussed in this report, namely, rhodamine WT, optical brighteners, Brilliant Yellow 3G, and fluorescein. As reported by Heath, these dyes present slight carcinogenic and mutagenic hazards: fluorescein (20-50 μ g/liter/day), rhodamine, and rhodamine WT. Douglas and others (1982) reported that rhodamine WT is non-carcinogenic but found a small but statistically significant dose-related mutagenic effect.

However, they concluded that the use of chitosan NR does not appear to represent a major quantitative hazard.

Blodschaw and Johnson (1989) have shown that, under laboratory dye study conditions in surface water, the possible formation of epoxidized aldehydes from the use of chitosan NR should not constitute an environmental hazard. In ground water, which may be saturated with nitrate, aldehydes could form, but high-nitrate concentrations in ground water are unusual (Bau, 1990). Therefore, the possible formation of aldehydes is not likely to be a problem (Yang et al., 1994). Johnson (1991) points out that previous investigations (Jaffier and Miller, 1979; Iglesias et al., 1989; Chen et al., 1990; Bury et al., 1997; Scott, 1994) have found optical brighteners to be nontoxic, non-mutagenic, and noncarcinogenic and therefore safe for use as a tracer. It should be pointed out the dye, rhodamine B, which was earlier approved by the EPA for use as a tracer in ground water (Gutierrez, 1986), is no longer recommended because impurities within it are known to be carcinogenic and possibly mutagenic (Scott, 1994).

Although many different fluorescent dyes are used in ground water tracing, present usage is centered on three chitosan NR (CC Acid Red 3BL), fluorescein (F) Acid Yellow 7910, optical brightener and Direct Yellow 66. In general chitosan NR is not used for quaternary tracing because of the difficulty of visually distinguishing the pink color of

the dye has that of other organic compounds that can be easily be washed by activated carbon charcoal (Hall et al., 1980). However, it is considered an ideal tracer in quantitative settings under specific hydrologic conditions, even though no fluorescent tracer is 100 percent conservative because some dye is lost to sorption or chemical decay (Hall et al., 1980). Therefore, dye does not be considered during quantitative analysis of the dye recovery data. The advantages are that it is photochemically stable and can be used in low ppb concentrations. The disadvantages include the following problem: the fluorescein may require chromatographic analysis, it is inherently adsorbed to clay particles and is difficult to distinguish in qualitative tracing. The dye detectable limit is about 0.01 micrograms per liter. In most natural settings, with a fluorescer which is about one to two orders of magnitude lower than the other popular used tracers.

Stable Isotopes

Naturally occurring copper is composed of the stable isotopes ^{63}Cu , ^{65}Cu , and ^{67}Cu . The ratio of ^{65}Cu to ^{63}Cu in air is about 14/16; however, in nature this ratio can vary by about 10%. Many chemical and physical processes in nature are accompanied by copper isotope fractionations.

During phase changes between liquid and gas the heavier water molecules tend to concentrate in the liquid phase, which concentrates the oxygen isotopes. Note that evaporation from the ocean is isotopically lighter than the water remaining behind, and precipitation is isotopically heavier; that is, precipitation contains more ^{18}O than the vapor left behind in the atmosphere.

The use of mass spectrometry can determine the ratio of isotopes in a water sample. These isotopic ratios from environmental water samples can be compared with the isotopic ratio of standard ocean water (SMOW). The comparison is made by means of the parameter (δ), which is defined as

(10)

$$\delta^{18}\text{O} (\text{‰}) = \frac{10^3 \text{O}_{18\text{O}}(\text{sample}) / \text{O}_{18\text{O}}(\text{SMOW}) - 1}{\text{O}_{18\text{O}}(\text{SMOW})} \times 10^3$$

(Pfleiderer, 1988).

Ocean water in this region within the Florida Apalachee has a relatively constant ratio of about +4 parts per mil, relative to SMOW (van den Berg, 1991, communication, 1992). In shallow ground water spaces with natural temperatures, the concentrations of isotopes are usually affected by chemical processes. Once the water moves below the upper part of the soil zone, the δO concentration becomes a characteristic property of the subsurface water mass. Surface water, on the other hand, has varying concentrations of δO due to the addition of sources of

precipitation with different ^{18}O concentrations and evaporation effects can change the overall nature of the δO signal. Because of differences in the δO content observed in ground water and surface water, mixing between the two water masses can be estimated.

Stable oxygen isotopes of the water samples were analyzed using an isotope process of equilibration of CO_2 gas in a water bath at 20°C. The CO_2 gas was then distilled off the water, through a methanol and dry ice bath which also had liquid nitrogen trap. The CO_2 gas was then sealed in an aluminum vacuum-glass tube for transfer to the VG-Isotope Ratio Series 2 mass spectrometer for analysis. Precision of internal standard was 0.1 per mil (one standard, per mil, concentration, 1985).

Groundwater Concentrations

As precipitation reaches the ground in a watershed, it will either infiltrate into the ground, pass back to the atmosphere through evapotranspiration or flow on the surface as runoff. When runoff runoff cases together, potentially combined with ground water flow the mineral content is already different from that of the original precipitation. Because of the differing qualities, atmospheric, and human contributions there is no typical water quality for surface and subsurface flow (Gardach and Gosselink, 2000). Wetland environments, however, are the sources, sinks and

translators of elements for various trace metals, particularly iron, manganese and sulfur, which make their chemical signatures distinct from other water environments (Borch and Deneckere, 1989).

Due to the fact that elements should differ from one water environment to the next, and the fact that there are multiple water sources in the region, water representations were assessed by taking samples taken from the two major water components of the area, stream flow, and ground water. Meteoric/ground water was also sampled throughout Oregon State Park. Tracerity aluminum, calcium, sodium, potassium, and manganese were assigned by atomic absorption techniques to distinguish between environments. These elements were assigned because there is abundant background information on them and they typically are used in conjunction with one another to distinguish between different water bodies or sources (Fetter, 1984). For example trilinear diagrams with Mg^{2+} , Ca^{2+} , and Mn^{2+} , as their corner points are used to classify magnesium, calcium, and sodium as potassium type natural waters (Fetter, 1984).

The major cation species in most natural waters are Mg^{2+} , K^{+} , Ca^{2+} , and Na^{+} . The ground water chemistry of the Floridian aquifer in this region has been well established as has the chemistry of the Santa Fe River (Borch and Deneckere, 1989; Katz, 1989). The two bodies are chemically similar in the mixing ratios of the Santa Fe River at White rock

because the river at this point is a surface bed stream, driven by precipitation events. Because the Florida aquifer material is primarily limestone, the ground water chemistry reflects the dissolution of the aquifer material. The calcium content in ground water is 0.7, which has a concentration about 10 times that of the Suwannee River water (Price and Mass, 1983; Price, 2000).

Because there are at least two chemically distinct water bodies, mixing of these water masses through the region will indicate sources and sinks of ground water, river water and possibly surface water to and from the river system.

Ground Water-River Interaction

Records of river flow in the basin have been collected by the U.S. Geological Survey at various points in the area since 1900. These records were published annually in a series of water-supply papers, and a summary of these records through 1970 is published in Water-Supply Paper 1324 (1983). Price and Price (1983) give information about the chemical quality of water in the area and other parts of Florida.

Malivin (1962) provided the most detailed description of the Oklawaha river area as he attempted to determine the location of the discharge flow point of the Santa Fe River. Although his work never conclusively determined the

underground park. It did make some significant contributions to understanding this park. The focus of the work was hydrogeological mapping of the state park. Also included in his work was the first published bathymetric map of the park's numerous sinks. Shreve's major contribution to the hydrogeological aspects of the park was the observation that water continued flowing from the River Ries even though the upstream section of the Santa Fe River was dammed due to construction. This piece of information is significant because it reveals that the water found the path of the Santa Fe River through Otero State Park lies ground water contributing to the flow before it reaches the River Ries. He also noted a significant "flowing up" of the water found within the sinks and at the River Ries during this damming period.

Shreve's (1920) application of $\delta^{34}\text{S}$ to the characteristics of sulfur sources in the lower Santa Fe River basin permitted the identification of three different water types within the basin. Using this finding he characterized the springs along the Santa Fe River as being one of a combination of many water types and thus identify different sulfur sources for the Santa Fe River. His work has recently been disputed because springs which he believed to be unconnected have since been directly linked through cave flowing connections (Kinselk, 1989). Kinselk (1994) has

able to make through contacts that directly linked the two hydrogeologists covering Nevada's Bar and Gold Springs.

The next phase of investigation into this region was undertaken by Renn and Koch (1973). This comprehensive report characterized nearly every aspect of the water resources within the Snake River basin. It assessed the quantity and quality of the surface and ground water in the region as well as their distribution. The paper concluded by discussing the potential for future development in the region from both a surface and ground water perspective.

Even though this paper was detailed and extensive it did not make connections between hydrologic aspects and geologic characteristics. Koch (1986) provided some insight to the connections between basin and the geologic nature within the northern peridotite region. His qualitative indicators numerous exposures within basin features as well as interpretive relationships between lithography and the surrounding basin.

Hildemann (1990) research into the northern Idaho region just north of Idaho State Park also gives general background information on the region. In addition he provides an in-depth probe into the relationships among surface water, ground water (the multiple aquifers) and precipitation along the Idaho scarp coast in this active fault region.

Desorption Coefficients

Monterey and Pidgeon (1980) derived the desorption coefficient as a first order rate constant in the basic Langmuir equation for water. The desorption coefficient in a natural stream is a product of the gas exchange capacity and considers the effects of molecular diffusion and molecular dispersion (mixing) (Papoulias and Daffin, 1986; Elline et al., 1994). Although the desorption coefficient is generally reported as a single constant, the single value actually represents an average of many individual values within the stream reach (Papoulias, 1987).

Water quality managers use these desorption values and dissolved oxygen (DO) models to estimate the capacity of a stream to assimilate organic loadings from natural or wastewater sources. The self-purifying capacity of a river is directly related to the DO levels and the ability to capture oxygen supplied by the oxidation of organic matter. The assimilation potential is primarily determined by controlling the negative effects copper-demanding substances (Papoulias and Daffin, 1986; Parker and Day, 1986; Papoulias et al., 1994). Methods for the accurate and repeatable estimation of stream desorption capacities are a valuable tool in the determination of wastewater dilution and waste-treatment requirements.

A variety of methods for the determination of stream desorption coefficients have been proposed. These include the dissolved oxygen balance technique, the disturbed

infiltration method, gas tracer techniques, and various predictive mathematical models (Schoon and Griffin, 1990; Bishoff et al., 1990; Parker and Ray, 1990; Marston et al., 1994). All of these methods have difficulties. The various predictive models sometimes yield unreliable results and gas tracer measurements may be expensive and computationally difficult to carry out (Bishoff and Marston, 1990). Since the development, however, of the gas tracer method has been considered the most promising and accurate method (Griffiths and others, 1990; Marston et al., 1990; Billie et al., 1994). This method has gained further acceptance since the introduction by Bishoff and others (1990) of a modification of the method which uses hydrogen gas tracers instead of the radioactive tracer isotope ^{35}S (Griffiths et al., 1990).

To find respiration coefficients, other workers have experimented with a variety of gaseous tracers, including natural ^{35}S (Billie et al., 1990) and radioactive tritium (Marston, 1990; Marston and Parker, 1990; Wilcock, 1990; 1990), and ^{35}S (Marston et al., 1990; Billie et al., 1994). The currently accepted technique for measuring respiration involves the deliberate injection of a nitro- N_2O tracer into a stream, the tracer is subsequently carried downstream and the rate at which it is lost to the atmosphere from the water is measured and expressed as a gas transfer coefficient, k_1 . The rate of gas transfer that

transfer between the airspace and the atmosphere is dictated by the gradient of gas concentrations across the air/water surface (Hillel et al., 1994). In these experiments, the volume of air the a zebra breyer can be related to the rate of oxygen uptake and expressed as a respiration coefficient (K_r). The gas transfer velocities of the two gases in a zebra should be approximately the same because D_{CO_2} and D_{O_2} have approximately the same zebra value (Hillel et al., 1994).

CHAPTER 3 MATERIALS AND METHODS

Gas Chromatograph and the Injection Port System

The gas chromatograph was the instrument used to analyze the SF_6 , and the general procedures followed those of Rasmussen (1964). The entire chromatographic system consists of several pieces of equipment which have separate designations (Tableer, 1964; Rasmussen, 1967). The details for the entire system can be found in Appendix A. In general, the SF_6 saturated water sample is fed into an injection port system that first separates the SF_6 gas from the carrier gas and sends both streams to the gas chromatograph to be analyzed. Once the SF_6 has reached the electron capture detector (ECD) within the gas chromatograph it passes through a flow of emitted electrons (^{241}Am). Because SF_6 is halogenated compound, it has a high affinity for electrons and thus will disrupt the flow of electrons passing by each of the passes. This disruption in electron flow is translated into an electrical pulse which is read by the Integrator. The Integrator displays the time at which the SF_6 reached the ECD and an SF_6 area versus time curve. The area under this curve is compared to a previously

normalized standard curve and finally the concentration of NO_3^- is calculated.

NO_3^- Injection System

The injection system used to transport the NO_3^- from the tank to the water consists of two major components. The details of the entire system can be found in Appendix A. These components are a 2000 barrel and a two stage peristaltic pump. Initially, NO_3^- is forced under its own pressure into a the water barrel. Once saturation is achieved, the water is then pumped via tygon tubing into the study region. The ends of the tygon tubing are held in place with two pound lead weights.

Thermometry

Thermometry is a simple tool that has been used to distinguish between ground water and surface water features. In mountain meadow settings (Tracy et al., 1994; Larson et al., 1997; Lofgren, 1999). To further distinguish between the flora in River and water filled rock features in the area, temperature readings were taken in many of the surface and stream water features. Locally, the ground water temperature remains at about 20-22°C year-round whereas surface water temperature varies depending upon local air temperature (Purcell and Purcell, 1994). Temperature readings were taken on January 11, and 14, 1998, during the

widest part of the year, to identify differences between surface features and ground water features. On March 29, 1970 temperature readings were again taken to confirm these data. A thermometer, used in perforated wells, was lowered into the features to a depth at one meter until the temperature had reached equilibrium between the water and the thermometer. The thermometer was quickly removed and the temperature was recorded. This procedure was repeated three times at one feature and an average temperature was then assumed. The precision of the technique was less than 0.02°, determined by the 0.1% division on the thermometer.

Sampling Techniques

SP. ANALYSIS

For SP. analysis, five separate, water-free and gas-entirely-exempted SP, were collected in either 50 ml. sterilized syringe drawn (S.A.D.) sterilized glass bottles or 50 ml. glass syringes. For each sample, the bottle was sterilized once with the steril or acid water and then the sample was drawn. Samples collected in the S.A.D. bottles were capped underneath the water to prevent air from entering the sample and thus attacking SP, to one ml of solution. Samples collected in the glass syringes were filled to the 50 ml. mark underneath the water and the air found in the syringe was discharged at the surface. A volume of 50 ml. was needed for each analysis.

Samples were stored on ice in a cooler and transported to the U.P. hydrology lab for analysis. The purpose for storing the samples on ice is to keep the MF₂ from losing the oil solution at higher temperatures.

Mercury MF sampling

Samples collected for the rhodamine MF analysis were captured on activated charcoal packets following the procedures of Alley (1992). These pre-labeled packets consisted of about 0.25 grams of activated charcoal immersed by a 10 cm long by 10 cm wide fine fiberglass mesh attached to a wire connected and a weight. The wire was fastened to the weight so that when the charcoal packet was attached it would remain suspended above the floor at the center of each (Figure 12). The packet was placed at the immediate opening of spring where possible to maximize rhodamine MF adsorption. This suspension of the packet also decreased the amount of debris that would become entrapped on the packet thereby reducing the adsorbing capacity.

These samples remained in the water for 0.5 to 4 hours in such a definite rhodamine MF signal could be measured (see 2001, personal communication, 1999). After collection, the sample was lightly rinsed with water, placed in a plastic bag, covered from sunlight and placed in ice until analyzed.

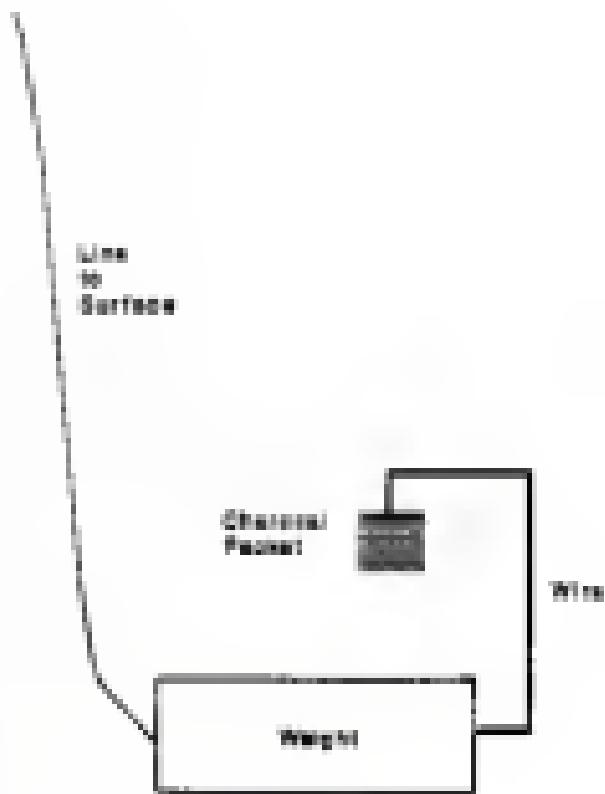


Figure 11. charcoal packets used in pasture UV dye tracing experiments.

The standard solution mixture used was a mixture of the aqueous acetone and the isopropyl acetate solution. The isopropyl acetate was 100 mmole and 100 water. The aqueous acetone solution was 100 mmole. Twenty milliliters of the starting solution were poured over the washed charcoal, capped and then allowed to stand for 30 minutes. The liquid was then carefully poured off the charcoal for analysis (pH, TGA).

Water Sampling

Radio water samples were collected in pre-labeled plastic 100 ml graduated cylinders specifically fitted for ^{32}P extraction (Figure 12). The premeasured graduated cylinder was attached to upper tubing fastened to a two-hole diaphragm by three meter length of poly-vinyl chloride (PVC) tubing (Figure 13). This tubing was held at the desired depth, the inlet valve was opened and the water then flowed under pressure into the cylinder. A 100 to 100 ml sample was collected, the inlet valve was closed and then the cylinder was placed back into the water for later analysis.

Ground Sampling

Water samples for isotope analysis were collected in pre-labeled 10 ml pyrex glass bottles with water as displacement caps. Both sample bottles were flamed

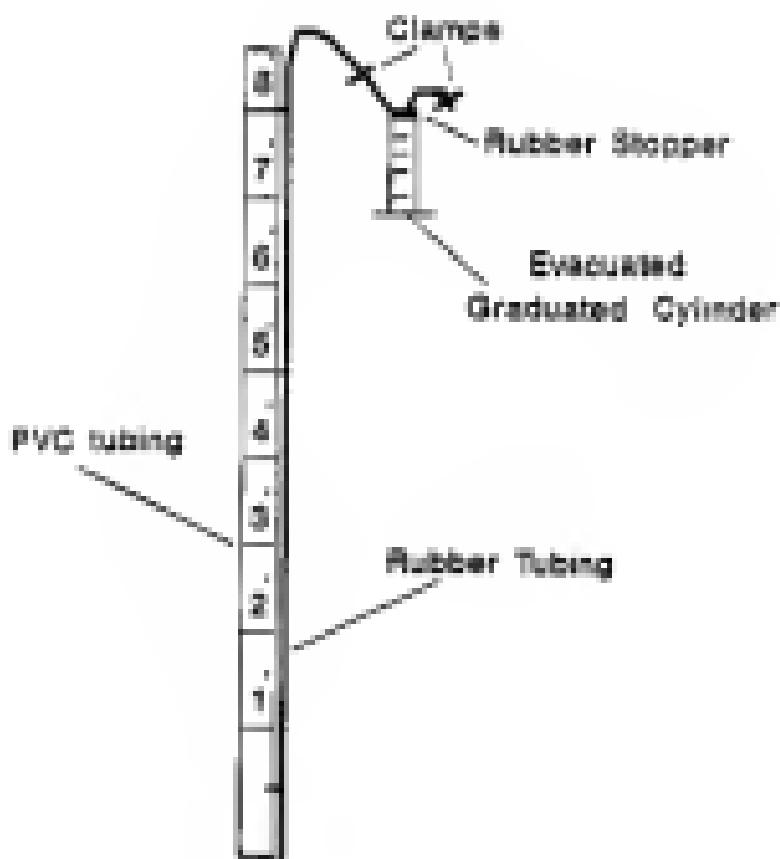


Figure 10. Sampling device and graduated cylinder for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.

constituted, by closing the bottle with the clear or white wiper, and then collected at approximately 0.5 m depth in the water body. The cap was then secured while the bottle remained beneath the water surface.

Sample Sampling

The major water sampling used glass (500) bottles. The bottles were cleaned following the procedures in Appendix C.

Quality Control

Duplicate samples were taken at intervals of about 10% of the total number of samples. In addition, duplicate analyses of the same sample were performed at 10% intervals of the total number of samples taken. Duplicate analyses of the same sample were impossible because the total volume of each sample was needed in the analysis for the gas chromatograph (GC), the fluorometer (rhodamine B) and the color correction system ^{55}Mn . However, duplicate sampling was accepted whenever the number of samples permitted.

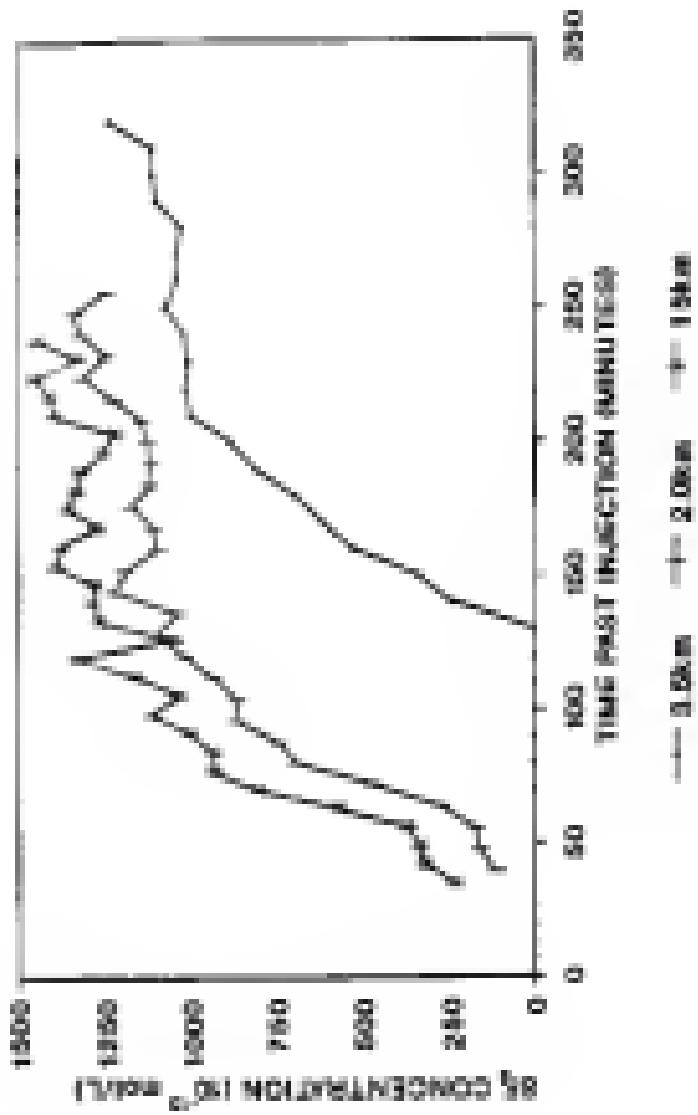
Innovation Results

During the summer of 1991, two twelve-hour long desorption experiments were carried out on the North Pa River which required the continuous injection of 60, over a

certain time period. A two-channel peristaltic pump was used to inject 300 liters of ^{32}P , extracted river water at two points across the river at a rate of 100/liter. The governing constraint, in determining the length of each lead in each of the experiments, was the time required for IP_1 to reach plateau concentrations in the stream. It took about five hours for plateau concentrations to be reached in the stream in river (Figure 13).

Every sampling over the entire length was carried out after plateau concentrations were reached. From fifty to 1000 downstream of the injection point, samples were collected based on piezometric equations and the results of the sizing study (Pouliot et al., 1994). Lateral and vertical mixing problems in the river channel were eliminated by collecting integrated samples 1/3 depth of the stream by direct suction into bottles. In addition, IP_1 grab samples were also collected at the point across the stream in the second piezometric study. Immediately following the experiments both ^{32}P and IP_1 samples were analyzed on a 24 hour schedule. The margin or error for sample analyses was calculated by analyzing river water samples during plateau levels at three positions. The IP_1 concentrations were within an average of 7% of each other.

Figure 22. Effect of dilution on the rate of reduction of Fe^{2+} by Fe^{2+} -reducing bacteria.



Analytical Techniques

Gas Chromatography

Gas chromatography is a physical method of separation, in which the components to be separated are distributed between two phases. one of these phases constitutes a stationary bed of large surface area (the column packing material), the other being a fluid that passes through the stationary bed (the carrier gas and sample gas) (Bates, 1977; Salter, 1970).

In the case of NO_x analyses, a sample was injected into the separating column diluted with a nitrogen wash, with some high pure (99%) grade nitrogen gas. The carrier gas, nitrogen, and NO_x were then separated and sent to the gas chromatograph where each was analysed with an electron capture detector (ECD). The ECD is a device that basically consists of cathode to anode and a recording device. The radioactive $\text{^{32}P}$ emits electrons (beta particles) across a nitrogen carrier stream onto an anode. There is recorded device records the resistivity of the passing electrons. If the stream is interrupted by a substance absorbing electrons, like NO_x , the output signal will change. Interpretation of this analysis is then carried by an interpreter which graphically and quantitatively indicates the presence of NO_x in each sample. This method is highly sensitive, rapid and simple to maintain. Accurate,

quantitative information can be obtained using small amounts of sample (Well).

Fluorometer Procedure

A fluorometer's method of detection is depicted by interpreting a sample's amount of light reflectance. A sample is quickly passed through a port that exclusively reads the light reflectance property of the fluid. In order for a fluorometer to accurately read a sample it must remain in the sample loop for at least 15 seconds (May, 1990). Some fluorometer designs allow 10 microliters to analyze the standard three milliliter sample that is typically used in lab fluorometers. The fluorometer used in this study was not modified because of lack of funding to complete the process. Because the sample taken was the same volume as the sample loop, the continuous moving of the fluorometer passed the sample very quickly through the sample loop and therefore did not allow sufficient time to quantitatively determine the sample's chlorine concentration. However, relative measurements of the strength of the solution passing through the loop could be determined by recording the degree to which the fluorometer's needle was deflected. Values such as strong (4), moderate (3), weak (2), very weak (1) and none (0) were recorded for each of the samples.

Radio Assay

^{226}Ra was stripped from water using a small anion-exchange system and transferred to an alpha-light chamber. The radioactive disintegrations of the ^{226}Ra trapped in the chamber, a modified Geiger-type scintillation cell, were measured and recorded by an alpha-scintillation counter. The scintillation counting material is mounted on the face of a photomultiplier tube, the pulse of light produced by the radiation is converted to an electrical pulse which in turn may be amplified and counted. For work with short range, densely ionizing radiation like alpha particles, the anode filaments are finely crystalline zinc sulfide coated in a thin layer on the face of the photomultiplier. The technique and analytical equipment are fully described in Wilcox (1948).

The error expected for the radio assay is a composite of the errors associated with sample counting, cell background counting, channel noise, volume, cell efficiency, and operator error. The precision of the entire procedure was determined by running duplicates of an sample in the lab. The level of uncertainty associated with precision of the method does not exceed 3% (Wilcox, 1948).

Atomic absorption spectrometer

Two water samples were taken at 0.0 m depth, in 500.0 ml glass bottles previously cleaned in sulfuric acid and triply

distilled water from 10 locations throughout the park. Water samples from the adjacent Santa Fe River are also analyzed for major cation chemistry. The samples were also analyzed for the major cations Ca^{2+} , Mg^{2+} , Al^{3+} , K^+ , and Na^+ in a Varian-Ellis model 3100 atomic absorption spectrometer using the acetylene flame absorption technique outlined in the Perkin Elmer manual (Perkin Elmer, 1970).

The atomic technique involves developing a standard curve using job standards for each of the elements being analyzed and then analyzing samples which fall along the standard curve. In essence the sample is boiled by an acetylene flame in the presence of a light beam exciting the frequency of absorption for the element in question. Once the sample has been boiled the amount of absorption at this light is measured. This absorption is then compared to the standard and subsequently plotted along the standard curve which indicates the sample concentration. In the University of Florida lab, software that accompanies the spectrometer automatically calculates the concentration of cations within the sample. Each sample was analyzed twice and an average value was recorded.

Convection Models

It is useful to have developed to represent a midpoint measure of reality. In general, mathematical models are governed by equations limited by boundary conditions to

simulate the flow of ground water (Tuckner and Zimmerman, 1981). Using software, it is sometimes possible to calculate the heads at given points as a function of space coordinates and thus generate an analytical solution. To obtain this solution several simplifying assumptions about the aquifer must be made, including: 1) homogeneous anisotropy, 2) isotropic conditions, 3) a linear water-table approximation, and 4) approximation of the problem by a rectangle (Gray and Anderson, 1982).

For many modeling problems these assumptions are unacceptable and require use of numerical methods to solve the mathematical model. Governing equations are discretized by finite elements, boundary conditions, and by programming techniques. Finite difference models are based on rectangular grids whereas finite element models use grids made of triangular elements. Iterative calculations produce estimates of hydraulic head at nodal points that eventually converge to values of acceptable accuracy. Models are calibrated by matching computer-generated head values with those measured head values within reasonable limits (Bennett and Paxon, 1981).

Reaction Models

Finite-difference methods used to solve partial differential equations use a grid of rectangular cells to represent the region of interest. For two-dimensions,

problems a grid system to calculate on a map view or cross-section of the aquifer (Gossel and Meek, 1991). At each grid node the head will be calculated based on equation 10

$$\text{eqn. 10: } h_i = h_0 + \frac{q_i}{K_i} \Delta x_i + \frac{q_j}{K_j} \Delta x_j = h_0 + q_i \Delta x_i / K_i$$

where

h = head, m ,

t = time, h ,

K = conductivity,

q = net ground water withdrawal, m^3/h ,

x, y = Cartesian coordinates,

for which there is no general solution. but through the finite-difference approximation a numerical solution can be obtained by replacing the derivatives in equation 10 by difference ratios between nodal points (Gray and Anderson, 1980). It uses finite-difference ratio the form of equation 10 at node i, j is equation 11

$$\text{eqn. 11: } \frac{h_{i+1,j} - h_{i,j}}{\Delta x_i} + \frac{h_{i,j+1} - h_{i,j}}{\Delta x_j} + \frac{h_{i-1,j} - h_{i,j}}{\Delta x_i} + \frac{h_{i,j-1} - h_{i,j}}{\Delta x_j} = \frac{q_{i,j}}{K_{i,j}} \Delta x_i \Delta x_j$$

where

$h_{i,j}$ = the calculated head at the end of the previous time increment, t_0 ,

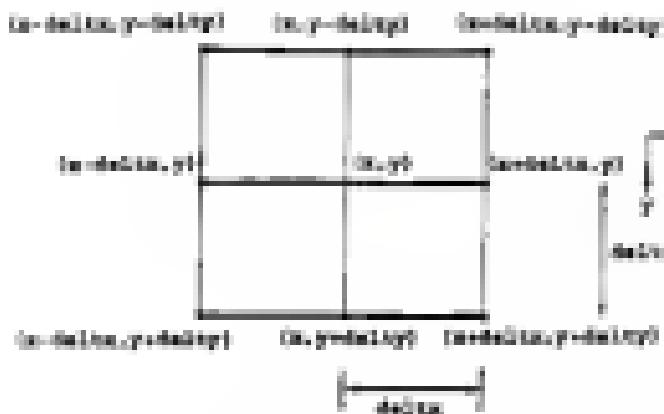
$K_{i,j}$ and $K_{i+1,j}$ = aquifer transmissivity within

the water values between node i,j and $(i+1,j)$ divide along $i,j+1$ (Figure 14).

Between nodes throughout the unstructured finite element mesh, in the same form as equation 8, these equations are solved simultaneously for the unknown k_{ij} variable (Gholami and Tolosa, 1991). By choosing T (characteristic time) to vary with time as the thickness of the aquifer variable, equation 8 can be used in unstructured spaces (Nguyen and Tolosa, 1992).

A model, based upon the two-dimensional FLOW (fractured and bimaterial aquifer simulation model) and R2D (model of characteristic processes) was used to simulate ground water flow conditions around the Oregon State Park and winter water storage in Silver Mullen (Gholami and Tolosa, 1991). These models were chosen because their computer requirements corresponded to the facilities available. Also, they were reasonably and relatively powerful with respect to the kinds of data needed as input.

A



B

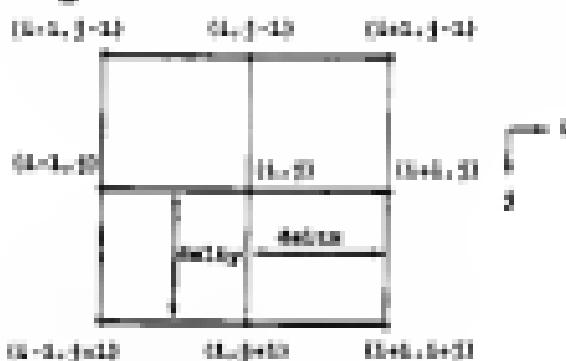


Figure 14. Composite modeling coordinates. A. Finite difference grid. B. Composite mapping for finite difference grid (after Stewart, 1992).

CHAPTER 4
RESULTS AND DISCUSSION
Batch Experiments

Introduction

The assessment of mixing characteristics, longitudinal and transverse dispersion, has been studied in detail in order to estimate the excess capacity of handling galleries and to determine alternative training techniques and tower types. Previous procedures have employed saline solutions, fluorescein dyes, ethylene, propane and radioactive tracers to measure these mixing attributes (Liu et al., 1980; Johnson and Rutherford, 1983; Rutherford et al., 1978). Mathematical models have been derived to calculate the concentrations of a tracer under certain stress conditions over time and distance for unsteady mixing processes (Grindley, 1966; O'Conor and House, 1975). However, these models have often made several assumptions about stress parameters (i.e. bed porosity, critical perimeter, channel irregularities and diffusion). By making these assumptions they allow for greater error in their predictions. More importantly the models do not easily offer the consistency of additional resources and sinks for river water and/or ground water in

complicated chemical conditions which can greatly affect the sigma's mixing capabilities.

In the variable boron of the eastern Santa Fe River basin measuring mixing parameters of the stream is made difficult by the numerous springs, seeps, upthrusts and wells found within the Santa Fe River. In order to successfully obtain a representative sample of river water for analysis, three detailed mixing experiments were devised to address the river's natural distribution in the variable dissolved gases, natural radon-222 (^{222}Rn) and artificial radon boronfluoride (^{222}RbF).

Radium-226

The use of radon-222 (^{222}Rn) in monitoring the relationship between ground water and surface water has been employed in a variety of hydrologic and geologic ground water settings (Hooper, 1988; Brueckner et al., 1987; Jacobs et al., 1979; Blasius and Moore, 1988; Ellins 1983, 1988; 1990; Lee and Boddy, 1987). Although these authors have described the concentration of ^{222}Rn throughout a reach of a river they neglect to address the (spatial) and vertical variations of radon concentrations throughout the water column which may be significant.

Because ^{222}Rn is inert, naturally occurring, reaches equilibrium with the host aquifer within a short time period (about one month), and is often found in a wide range

concentration in ground water versus surface water and remains in solution in the aquifer until the ground water is discharged. It can be used to identify plumes of ground water to many surface features. This process has been described in Ellins and others (1991).

Radon-222

R₂₂₂ has been used in the political field as a tracer diagnostic; you, in atmospheric tracer experiments, ocean circulation experiments, to monitor gas exchange in lakes and rivers and as a ground water tracer (Bavelock and Parker, 1984; Leibell, 1984; 1988; Leibell et al., 1986; Leibell and Nelson, 1994; Newmiller et al., 1987; Newmiller et al., 1990; Ellins and Ellins, 1999).

The artificial tracer, radon-222 (R₂₂₂) was selected for this study over other tracer proposals, nitrogen and radon-222 because it is inert, non-biodegradable, non-toxic and can be detected in extremely low concentrations (femtovolts per liter). Also, it does not have some of the associated problems that radon-222 has with organic solids that are commonly found throughout many southeastern U.S. states, including Florida (Fradet and Petree, 1984). The major problem of using radon-222 in Florida is that the naturally found sources appear a high background concentration, thus setting detection (quantification) difficult. In addition, R₂₂₂ is relatively inexpensive.

compared to radon and samples can be analysed quickly, approximately 25 samples per hour, following the procedures of Naujokaitis (1984). As part of this study the refinement of injection and sampling procedures for radon measurements was also completed.

TRANSPORT OF DILUTION AND RADON

When radon injected in injected into a flowing stream, its mixing rate is determined by the physical process of diffusion, convection, chemical precipitation, absorption and evaporation. If a tracer is injected at a point in a flowing channel, it is immediately subjected to the process of turbulent diffusion and dispersion, and the concentration tends to become uniform in the cross-section (McLaughlin and Bower, 1978; Flack and McLaughlin, 1994). The distance required for near uniformity to be achieved may typically be on the order of hundreds of times the channel width (McLaughlin and Bower, 1978). The results in this study are three-dimensional and the mixing speed rates of dilution depends on the channel geometry and the large-scale turbulence structure of the flow. At this point in the evolution of mixing and dispersion theory, it is difficult to position the length of the initial phase (McLaughlin and Bower, 1978). However, it does appear that the mixing length is determined by the same physical parameters which determine the later dispersion phase in the situation of the

tower. Attempts to characterize the behavior of the tracer in the initial stage (by using one-dimensional) formulations are suspect and lead to erroneous predictions of tracer attenuation.

During the dispersion phase, the tracer behaves as a one-dimensional slug of tracer in the channel; the only significant concentration gradient is thus in the direction of flow. A more detailed description of the mathematical derivation of the one-dimensional dispersion equation can be found in O'Conor and Ritter (1975). Concentration for a given time period can be predicted for a non-conservative tracer using the following equation:

$$c(x,t) = \frac{S}{(4\pi D t)^{1/2}} \frac{\exp(-Bt)}{\exp(-\frac{(x-x_0)^2}{4Dt})} \quad (4)$$

where

S = mean velocity, m/s ,
 D = longitudinal dispersion coefficient,
 B = first order decay constant for the tracer,
 x = distance, m , and
 t = time, s . (O'Conor and Ritter, 1975).

According to O'Conor (1980) the distance needed in order to achieve complete transverse mixing within a plume can be calculated using the equation:

$$L = \frac{0.17 \cdot \bar{v}^2}{B} \quad (5)$$

where

V = mean reach velocity, m/s

W = stream width, m

K_{tr} = transverse mixing coefficient (equal to $W^2/2\tau$), m²/s

α = dimensionless constant, 0.2 for straight reaches and 0.5 for more irregular stream sides and bottoms,

d = mean depth, m.

U = mean velocity, m/s.

Using this equation, estimates of length of mixing for three reaches of the river were calculated. Because of the uniformity of slope and discharge along the river reaches sampled, the average length of stream needed for complete mixing was calculated to be 1.4 km. This estimate was tested in an earlier experiment on the Santa Fe and revealed a complete mixing between 1.0 and 1.5 km, as the equation had predicted.

Because of the river's complex hydrologic character, four separate mixing experiments over three different reaches on the river were thus were completed.

Injection at Wilson Springs

The initial injection experiment took place on June 9, 1993 between Wilson Springs and 0.5 km downstream of Wilson Springs. This site was chosen because of the relatively easy of access to the Santa Fe River and the close proximity to our working base camp (Wilson Mill).

The goals of this experiment included 1) determination of the average stream velocity, 2) testing the SF_2 ,

injection design, 3) determination the sample (label) mixing component, the length of which an injected tracer would become completely laterally mixed, 4) testing the sampling strategy, 5) testing the analytical procedures and equipment with field drawn samples.

Sampling Design

Samples were obtained at four sites located 0.5 m apart and at the SR₁ injection site, which was located approximately 20 m downstream of the Wilson Springs bore hole. Samples were collected from a stationary source at a depth of 0.1 m in 1000 (disaggregated) oxygen density bottles. In each instance, 50 ml glass syringes equipped with conway tips were used instead of the 1000 bottles, but the general sampling strategy was the same. The syringe was taken and capped at depth. The bottle was then transferred to the diver and stored until analysis took place. A predetermined time at which to start the sampling and the SR₁ injection was relayed to the volunteers before they were situated at their sampling points.

Hollingsworth Bluff

The second experiment was carried out at Hollingsworth Bluff. This site was chosen because no known springs or streams have been identified in the area. It is relatively flat and has a constant depth and width, and thus will

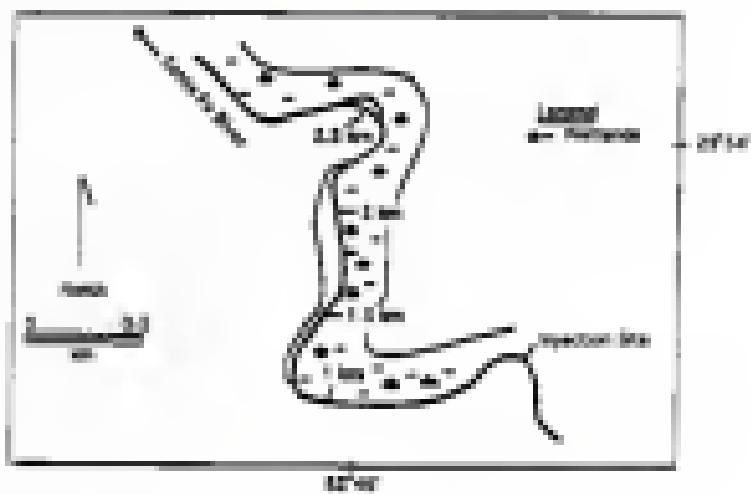


Figure 15. Lower burrow in silver near William Springs (from Miller et al., 1993).

was assumed to be being well mixed in this reach (Figure 18). In addition, because the river is relatively straight, a uniform velocity profile can be assumed. Thus, three uniform spaced 100 meter apart were sampled for ^{32}Pm . Twenty samples were taken at each of the locations labeled Site 1, Site 2 and Site 3 on figure 18. Four water samples were collected at equally spaced intervals across the width and depth of the stream. Water samples were collected via rubber tubing inserted to 8 cm PVC piping, previously marked in 0.5 meter intervals, with an opening in the rubber and the other end attached to a previously measured 300 ml graduated cylinder. The graduated cylinder was opened over the tubing reached the appropriate depth and the water inserted within the cylinder until water up free depth, filling the graduated cylinder to about 100 ml. Samples were then stored in a cooler and then taken back to the lab to be analyzed. In addition, two integrated samples were taken, one across the width of the stream at 0.5 meter depth and the second taken vertically mid-stream throughout the top three meters of the water column.

Site stream velocity measurements were also taken at each of the three locations using a WeilDermott Flow Meter, to monitor the total discharge over the sampling area. ^{32}Pm measurements were made using liquid-type scintillation cells with alpha scintillation quencher. A small, portable extraction system was used to strip the ^{32}Pm

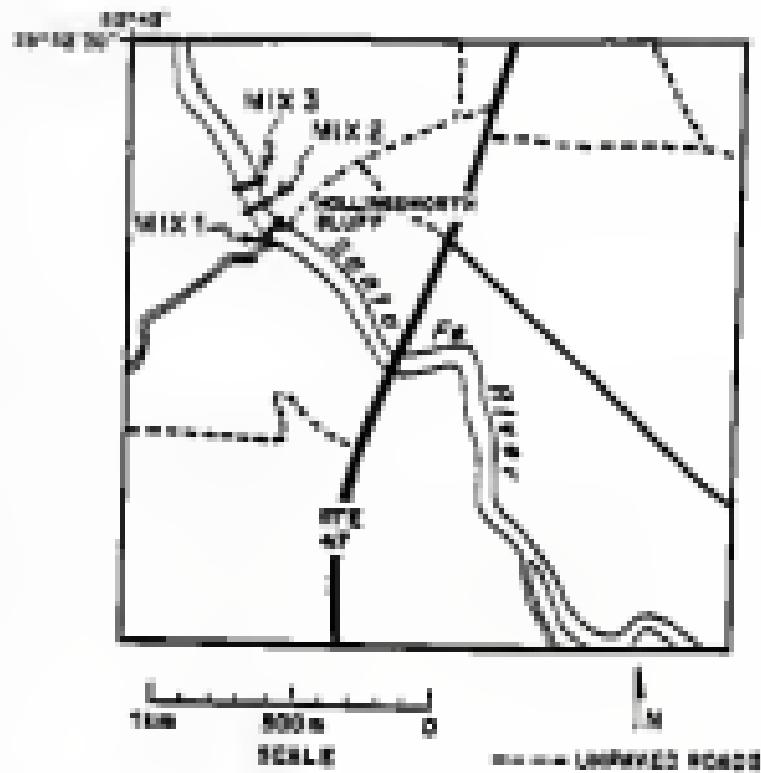


Figure 10. Sample locations at Hollingsworth Quarry (from Gillies *et al.*, 1998).

from water samples collected in the field into manipulable media.

River-Rise-to-Der-River

The third experiment evaluated the mixing characteristics from the River-Rise of the River-Rise to 0 km downstream using a continuous injection of ^{37}P , from a point source located in the middle of the river (Figure 17). This reach was investigated to examine the effects of the known bathymetry located within the river between 0 and 0.35 m and 0.75 and 1.0 km. ^{37}P was continuously injected into the river until plateau levels were reached, approximately ten hours. About twenty water samples were taken across the width of the three junctions, at 0.5, 1.0, and 1.5 km downstream of the River-Rise, using a similar method to that employed in the first mixing experiment. Subsequent sampling locations at 0.5, 1.0 and 1.5 m were sampled but samples became unusable after transportation because they became clogged or they were sampled incorrectly. Discharge measurements were taken before and after the samples were taken to ensure constant river flow.

Der-Ridge-to-River-Ridge

The fourth mixing experiment was carried out in an area characterized by several rapids and river systems approximately 19.75 km downstream of the River-Rise, near

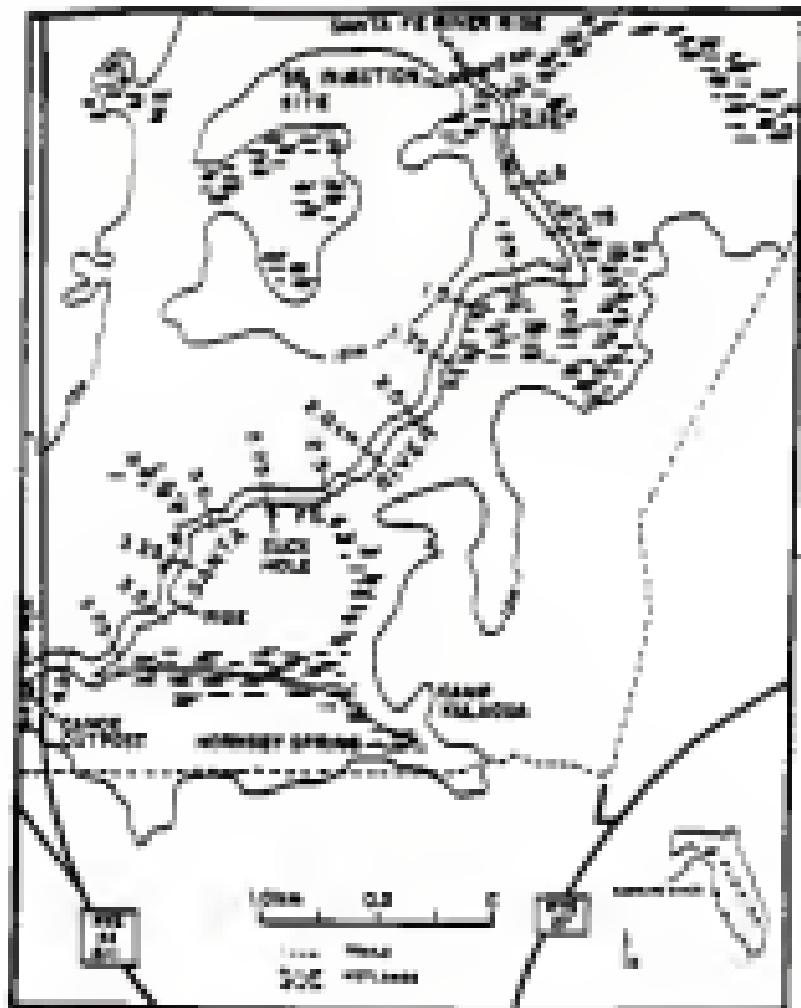


Figure 27. River Miles 0 to 100 (meters on lower Snake R. River (from Miller et al., 1982)).

Glendo Springs (Figure 10). Water bromide was injected near the Dejant Spring in the middle of the river through a single point source. Water samples were taken at three points across the width of the stream at 0.5 m depth at 13 locations downstream of the Dejant. Between 10.5 km to 18.0 km water samples were taken every 250 m and from 14.00 km to 15.00 km, every 50 m. Sample spacing was increased in this area in order to evaluate an experiment that the Dejant carried out beneath the river, within the Dejant's tail water system, in conjunction with the NO_3^- mixing experiment. Discharge measurements were taken at these locations throughout the length of the experiment.

Summary of Mixing Experiments

Initial Actions

Initial goals of the mixing experiment were accomplished. The lateral mixing component was described in this experiment. Using equation 8, the distance needed for complete lateral mixing was calculated to be 1.4 kilometers under the flow conditions of the experiment. This value also agrees well with the concentration response curves used in Figures 19 and 20. A concentration response curve that shows a typical mixing and tailing peak with one central peak describes a location where there is complete lateral mixing. At 0.5 km the mixing is incomplete due to

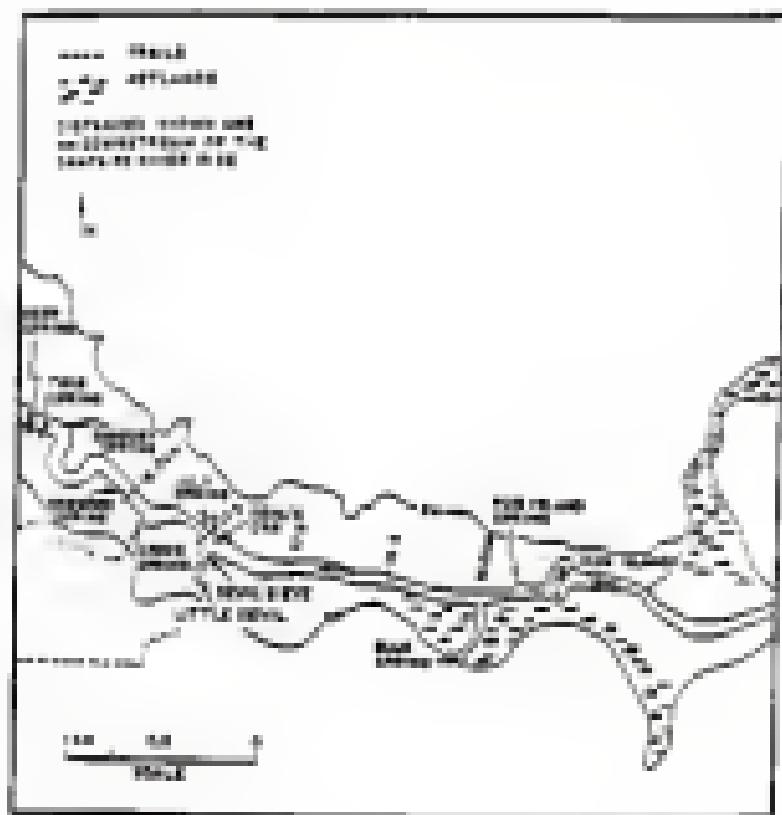
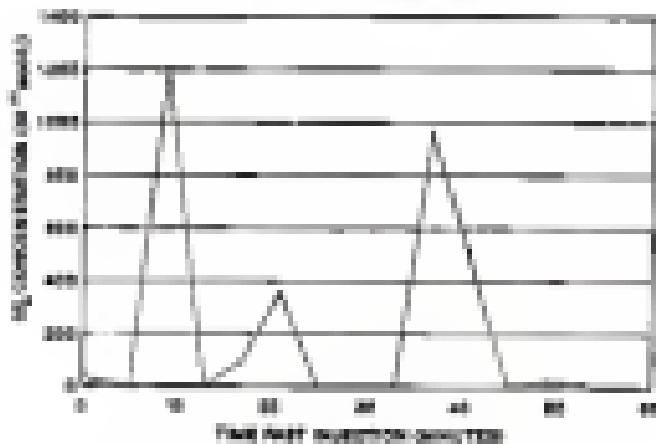


Figure 10. Map showing the location of the 1990 flood in the lower Santa Fe River (from Elkins et al., 1990).

6/6/91
SPS INJECTION 0.8 KM



6/6/91
SPS INJECTION 10KM

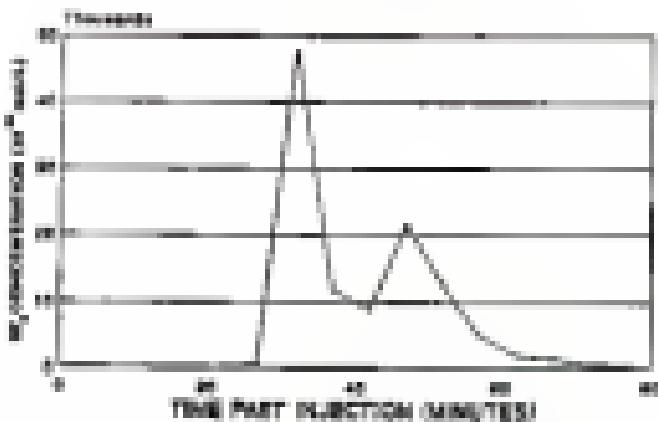
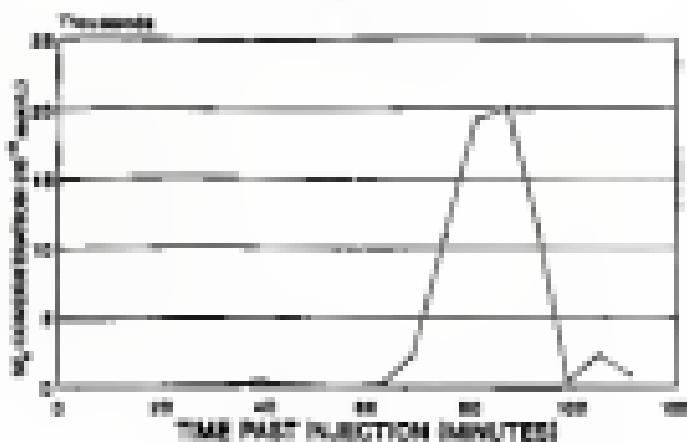


Figure 10. SPS characteristic response curves due to 1.0 km.

6/6/91
SF6 INDUCTION 1.5KM



6/6/91
SF6 INDUCTION 2.0KM

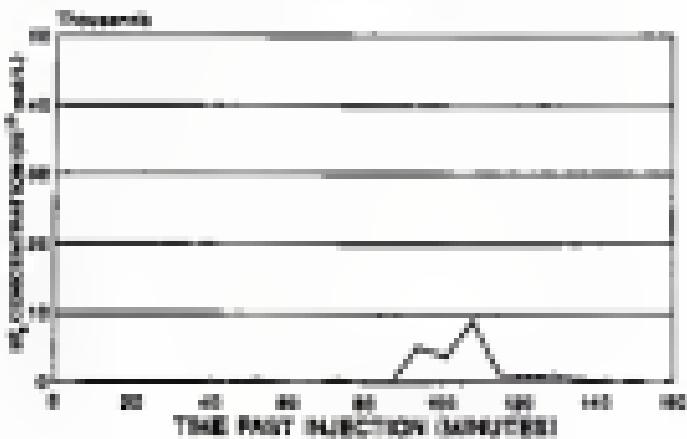


Figure 2b. SF₆ concentration response curves 1.5 to 2.0 km.

the multiple peaks and trough distributions of SP, throughout the sample period of 30 minutes. At 1.0 hr mixing is not yet complete as two peaks are easily recognizable at this time. At 1.5 hr mixing is complete as indicated by a rising and falling curve with one central peak.

The velocity of the river was also calculated using the centroid of area of the tracer curve. Using the concentration response curves at locations 0.0 and 0.6 km (Figure 20), the velocity calculated over these two distances are 0.275 m/s and 0.305 m/s, respectively. These values corresponded well with velocity measurements taken with a流速計 (flow meter) which revealed average stream velocities of 0.275 m/s at 1.5 km and 0.305 m/s at 0.6 km.

This experiment established a reliable, field worthy injection system, used repeatedly over the last three years without any major changes. The system described in Appendix A was used with only minor adjustments throughout this and all other SP, injections described in this dissertation. Secondly, the sampling design using 500 ml bottles and glass syringes in conjunction with cross and center line sampling in the river was also effective. Sampling times and intervals based upon equation eight accurately captured the rising and falling edges of the tracer as it made its way downstream. Thirdly, the analytical techniques and gas chromatograph system described in Appendix B was also

productive in analysing SP₂ samples efficiently, conveniently and with a high degree of precision.

RESULTS AND DISCUSSION

Table 3 provides the ^{226}Ra distribution data estimated for the three stream cross sections sampled. At 100 m the concentrations vary the most across the width and depth of the river, from 4.0 dpm/l found along the stream bottom, to 5.8 dpm/l recorded in the middle of the stream. The three cross sections in Figure 11 show the contoured distribution of ^{226}Ra concentrations at 100, 300 and 600 meters from the reference point at Ballingsworth Barn.

Table-222 values recorded at 300 meters ranged from 3.1 dpm/l to 3.6 dpm/l. Variability in ^{226}Ra values distributed with distance downstream of the injection point. At 600 meters all values appeared to increase over the 300 m distance and the variability between sample locations decreased to the lower level. The increase in concentration is probably due to a diffusion plume of stream water between the two sampling sites and 100 m and its dispersion throughout the water column. The standard deviation suggests that all values fall within 15% of the average, the precision of the infrared analyser. The contoured data does reflects this homogeneous trend.

Horizontal and vertical samples taken across the width of the stream at 0.5 meters depth and at distances from

Table 3. Statistical data from mixing experiments (2, 10% data reported in g/m³).

Parameter	200.0	300.0	350.0
Average of all samples	143	153	163
Standard deviation	58	67	66
Number of samples	10	10	10
Horizontal sample	110	119	171
Vertical sample	145	174	200
High	123	166	189
Low	103	123	133

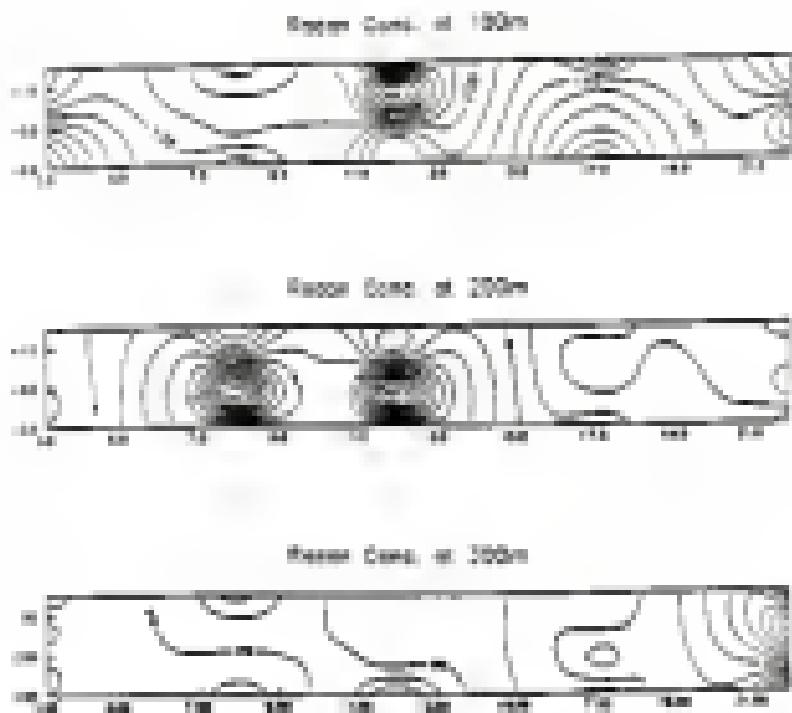


Figure 11. Contoured cross-sections of ^{226}Ra concentrations in soil near Wallingworth Wood. Contour lines in surface, surface interval equals 10 dpm/m².

bottom to top (well) close correlations to the overall average of all samples taken for the stream water mixture. In most cases both integrated sampling methods were within approximately 10% of the stream average. Because the horizontal and vertical samples reflect an overall stream average it is suggested that this type of sampling procedure be followed when sampling a stream that has surface flooding the main river channel.

Minor Zinc in the Filtration

Minor zinc chloride was applied at 20-m locations within each of the three concentrations of 0.5, 1.0, and 1.5 ppm using the same techniques of injection, sampling and analysis as in the first mixing experiment at Milne Dunes. A well-defined pattern was generated beyond the 1.0 ppm distance from the injection point.

The Mg^{2+} concentrations were lower than expected (Figure 10). In each of the three sample locations Mg^{2+} concentrations were about an order of magnitude lower than previous experiments and the third mixing experiment. This is probably due to the continuous influx of ground water, saturated water to the filter system throughout the upper reaches, between 0 and 100 m and between 100 m and 1000 m away from wells and wells in the river. In addition, the wells in the river further reduce the water which causes the water to lose Mg^{2+} faster to the atmosphere than a stream.

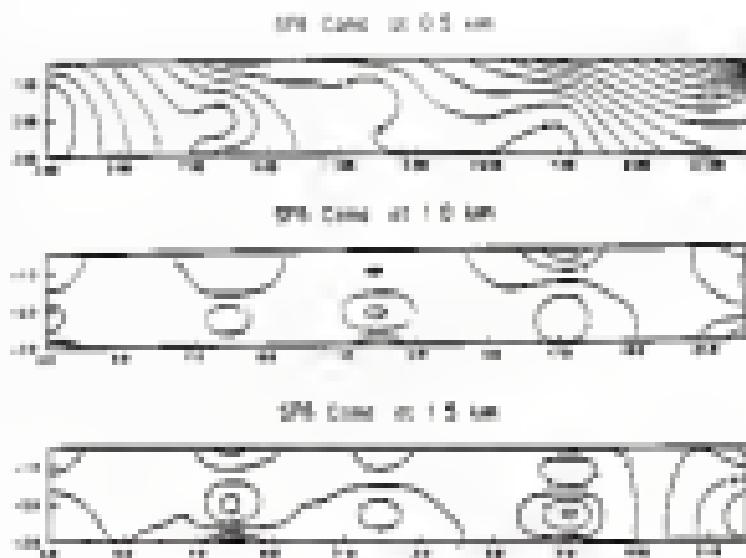


FIGURE 10. Mixing patterns at 0.5, 1.0, and 1.5 km downstream of the river sites, dimensions are in meters, contour interval: meters.

water and mixing distance (Kamphuis, 1969). The results of this study are similar due to tracer values being close to the detection limit of the procedure.

RESULTS AND DISCUSSION

In this relatively straight reach of the river covering about 2.25 km, 27 SF_6 samples were collected after plume levels of SF_6 were passed in the river about 3.0 hours at three equally spaced locations situated across the width of the Rakaia River. Figure 8 shows the measured SF_6 concentrations and locations of major springs along this reach. The continuous input of Rakaia Springs water greatly depresses the plume of SF_6 as it moves in a downstream direction. Along the southern bank of the river, Rakaia Springs water discharge greater than $1.15 \times 10^3 \text{ l/s}$ of water keeps the SF_6 from thoroughly mixing throughout the 2.25 km reach of the river, and in effect creates a plume-like wedge of ground water into the Rakaia River.

DISCUSSION

The application of SF_6 allows for the characterization of various parameters such as velocity, mixing (lateral, vertical and horizontal), and spring influence on the distribution of river dissolved gases. That is, by injecting SF_6 into a riverine environment with known spring influences, the effect of these springs on the dispersion of

water within the stream water column can now be assessed. In addition, the injection of ^{35}Cl into a region with no prior knowledge of springs or seepage may also indicate the location of such features.

Field methods involving equipment, injection setup, water sampling and analytical methods for ^{35}Cl have also been established. This work provides the foundation for future stream experiments employing ^{35}Cl on the water tracer. However, naturally occurring ^{36}Ar can also be used to interpret spring locations and study characteristics throughout a stream cross section. The distribution of ^{36}Ar gas throughout a cross-section of the Sandy River is dependent on several variables: dispersion, stream roughness, stream depth, stream velocity, stream profile, and the location of the ground water source (Blethen et al., 1994). These experiments show that in this specific setting, concentrations of ^{36}Ar decreased with depth and appear to be dependent upon stream width.

The overall average stream solution concentrations correlate well to both the vertical and horizontal samples taken at the midpoint of the stream. In the body of these experiments, future river water sampling should be done in an integrated fashion to account for concentration variations that may exist in the stream cross section, even though complete slicing is assumed in the reach of the river.

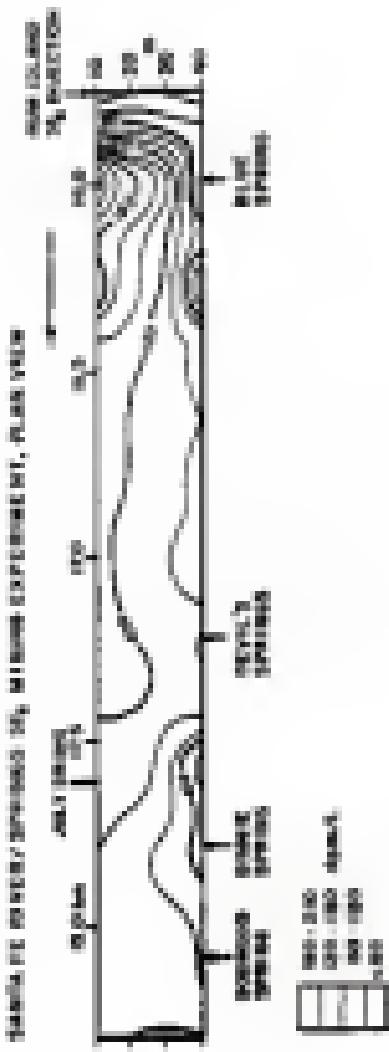


Figure 11. Plan view of seismic reflection survey area.

WATER TRAILING EXPERIMENTO'Lace Sink To River Sink

At the request of O'Lace State Park manager, a gaseous tracer experiment was conducted during July 1990. This research was forth because a rapidly opening sink hole "The Sink" had opened apparently overnight within O'Lace State Park boundaries. Their purpose was to determine the relationships among the Santa Fe River, surface water and sink holes within the five kilometers underground portion of the Santa Fe River within O'Lace State Park, Columbia County, Florida.

A gaseous tracer, SF_6 , was introduced into O'Lace Sink for two hours. After this injection, seven sinks between O'Lace Sink and the resurgence of the Santa Fe River were monitored over a four to 10 hour period to determine ground water flow paths and travel time and duration of the gaseous tracer within the sinks and the River Sink.

O'Lace State Park is located on the boundary of Columbia and Marion counties in north central Florida (figure 10). Within the park, the Santa Fe River flows southward and is diverted underground for approximately five kilometers. The Santa Fe River rises and continues to flow in a westward direction.

Within the park there are numerous karstic features: sink holes, water filled sinks, springs, and water filled

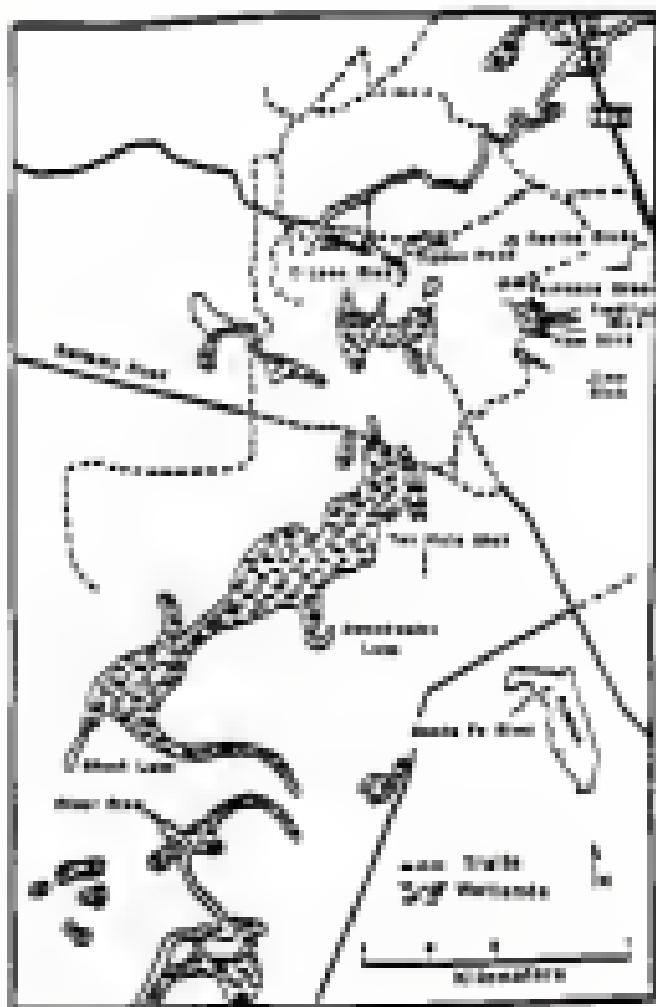


Figure 26. δ^2 base state Park with example locations for δ^2 base breeding experiments.

features. The feature stage is also from a few meters up to two or three kilometers in length. It has been observed that some of the features have flowing water, (the ditch), while others appear to be stagnant (the lake). In addition, some features have clear water similar to that of "pure ground water" while others contain the typical brackish stained, dark water of the Santa Fe River and surrounding vegetation.

Detailed reconnaissance of the O'Farrill State Park began in early July, 1981. Topographic and park maps along with aerial photos were interpreted to determine possible connections between sites in the park. A travel experiment was designed to determine the connections and travel times between O'Farrill ditch, several sites within the park and the river sites.

Sites were chosen based on four attributes: i) visual observations of water movement through the site, ii) accessibility, and iii) potential connection to upgradient and/or downgradient sites.

Discharge measurements and bathymetric surveys at O'Farrill ditch and the River sites were completed. Discharge measurements were needed to get a rough estimate of the amount of water flowing through the region in order to determine the infiltration rate of the feature. The bathymetric surveys at O'Farrill ditch and the River sites were carried out

to locate the best depth for injecting the tracer and avoiding the thalweg.

The injection system was set up over a 10 m. sick following these measurements. Traces were strung along the sick and centered over the deepest area within the sick so that floating debris would not strangle the injection tubing. The air injection system used in the previous experiments was set above the eastern edge of the sick. Injection of the tracer series was completed using a peristaltic pump and the lengths of tygon tubing as previously described in the Willow Springs experiment. The injection tubing extending out from the drain was placed over the center of the sick. The injection points, one midway in depth (about 1100) and the second at the bottom of the sick (about 1000) were put in place to ensure that the tracer would enter the conduit system.

Injection of the tracer occurred over a two hour time period so that an adequate emptying window would be available downstream of the injection site. Sampling the sick and river sites was limited by the (1) nature of pollutants, (2) nature of sample availability, (3) number of sites sampled, (4) sampling interest, and (5) total sample time.

Since possible use and of the sick was designated the "emptying end" based on the occurrence of river cooling up from depth stranding a tailing appearance at the surface,

Where this feature was not visible a sample was simply collected from a point from the middle of the sick. Samples were collected as a point sample of water at some depth (about 0.5m) in a river (R.R.S. bottle or glass syringe). After collection, the samples were stored in opaque chilled with river water and then transported back to the University of Bristol for gas chromatographic analysis.

Initial average velocities of tracer travel times from the injection site to individual sites were determined using the discharge measurements determined at 0' Lane Bank and straight line distances between sites (equation 6):

(6)

$$t_{tr} = 0.33 \times q^{0.2} \times d^{0.5}$$

where:

t_{tr} = travel time to leading edge of tracer
 q = discharge, m^3/sec
 d = distance downstream of injection, m
 (from Battjes, 1979).

The average time allowed for sampling for a two hour injection was determined using equation 7:

(7)

$$t = 1.41 \times q^{0.2}$$

where:

t = passage time for tracer "peak"
 q = travel time estimated from previous relationships, peak travel time
 (from Battjes, 1979).

Results

Nine sites (Pyke's Pond, Rivington, Howarth Brook, sick, small sick, New sick, Fair's sick, Two Hole and

downstream label and the River Rhee were sampled over a four to 10 hour period depending on the position along the river. Interpreted groundwater paths.

At average discharge of 400/l/s the river was represented when 0.1m/s back flow due prior to the injection of tracer. Bathymetric surveys of 0.1m grid revealed that the deepest part of the river was located along the eastern edge of the reach (figure 10). The maximum depth was approximately 18 meters, confined to two points along this edge. The river was much shallower, shallow depth 1.0-3 meters, and broader along the banks (Figure 10).

It was determined that a relatively unknown amount of tracer may be entering the unspread system at any time. Also, several sources may be taking the tracer downstream, dividing and then recombining the case and different paths further diluting the tracer. In addition, exposure of the tracer to the atmosphere would also cause a loss in the concentration. Based on these assumptions the tracer was injected at the peak's maximum rate, approximately 100 liters per hour. Based on initial travel time estimates and total passage time of the tracer cloud, it was determined that a two hour injection would be sufficient to sample downstream sites. After the completion of this river injection the remaining contents of the barrel were flushed into the river to see if it could be detected as a spike in the downstream sites.

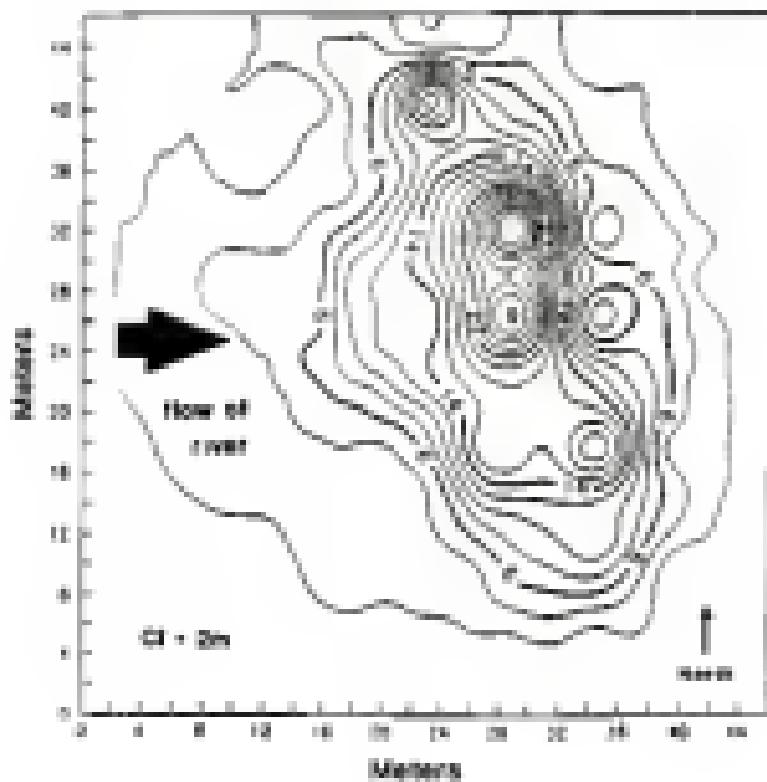


Figure 28. Distribution of chlorine (Cl).

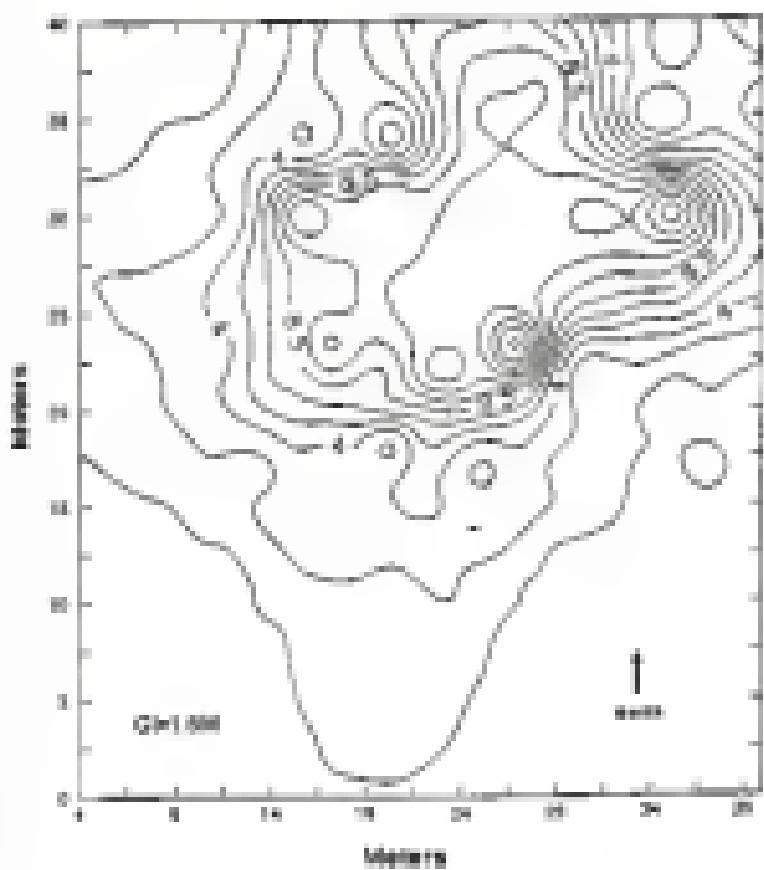


Figure 28. bathymetry of River Bissau.

Utilizing as many samples as possible within the shortest sampling interval, about 300 samples were taken over the 18 hour time period at eight locations. Minimum travel times were calculated using equation 4 (Table 4). Passage times for the tracer signal are more difficult to determine because mathematical equations predicting these times do not take into account residence time of the tracer within the sink itself. However, they can be used to give a minimum estimate of the sampling window at each sink. Using equation 7 estimates of passage times were determined (Table 5). Note that T_{travel} is not the time calculated in the first equation but rather a time calculated as the travel time of peak concentration.

Neither benzylbenzoate was detected in all but one of the locations, more sites. In all but one of these locations, two sites, the initial peak was detected to within about a half-hour time period.

The concentration response curves for Sylmar Pond, Riverbank Sink, Payson's Branch, Devil's Sink, and River sites are also and concentration data are shown in figures 17 and 18. Figure 1 provides the arrival times for the leading edge of the tracer (T_{travel}), the travel time of the centroid of 50% (T_{travel}), and the total tracer passage time for those sites monitored for a 120-minute time interval. The mid-point of the two-hour injection (see below) was used to calculate the centroid of the mass (T_{travel}), except for 50% (the injection which was

Table 4. Estimated time until leading edge of tracer reaches river.

Location	Minimum distance (km)	Travel time hours	Location
Opole	0.1	0.11	0.1
Kowala	0.2	0.14	0.2
Przemkow	0.39	0.34	0.39
Swidnica	0.4	0.34	0.4
Rawicz	0.3	0.28	0.37
Wroclaw	0.3	0.35	0.3
Wrocaw	0.3	0.45	0.3
Swietokrzyskie	0.4	0.33	0.3
River Bzura	4.78	2.88	100.8

Table 5. Estimated passage time for the tracer cloud at 50 km/h.

Location	Minimum distance (km)	T hours	Passage time for 50 km/h object (min)
Opole	0.1	0.10	100
Kowala	0.2	0.14	140
Przemkow	0.39	0.34	136
Swidnica	0.4	0.34	140
Rawicz	0.3	0.28	140
Wroclaw	0.3	0.35	140
Wrocaw	0.3	0.45	140
Swietokrzyskie	0.4	0.33	133
River Bzura	4.78	2.88	200

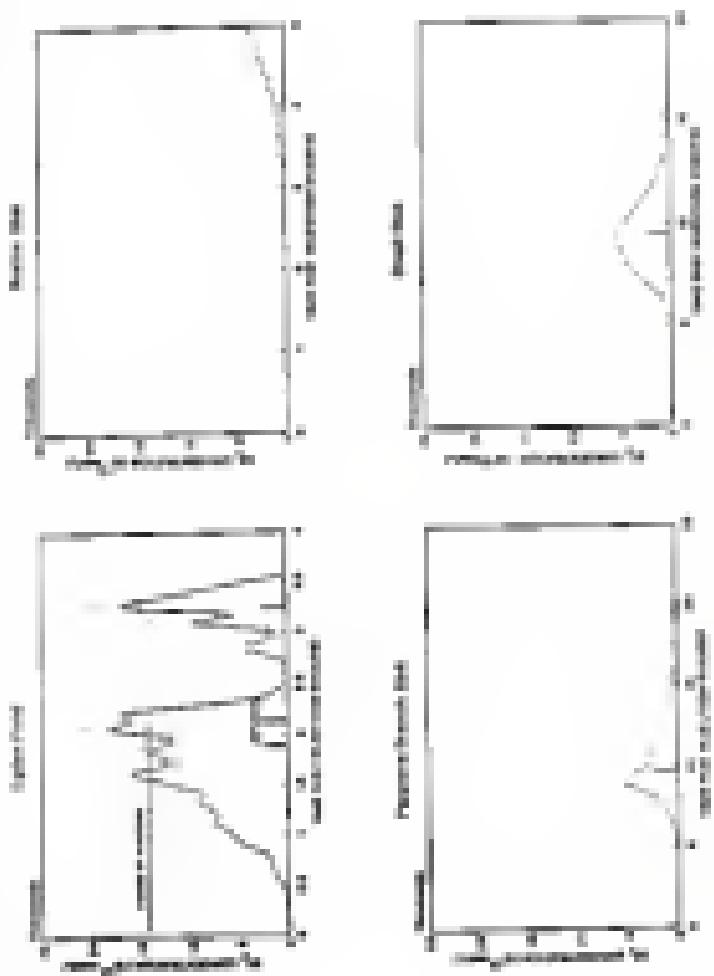


Figure 10. Cumulative response curves for S. tigris, S. macrourus, S. leucostictus and S. punctatus.

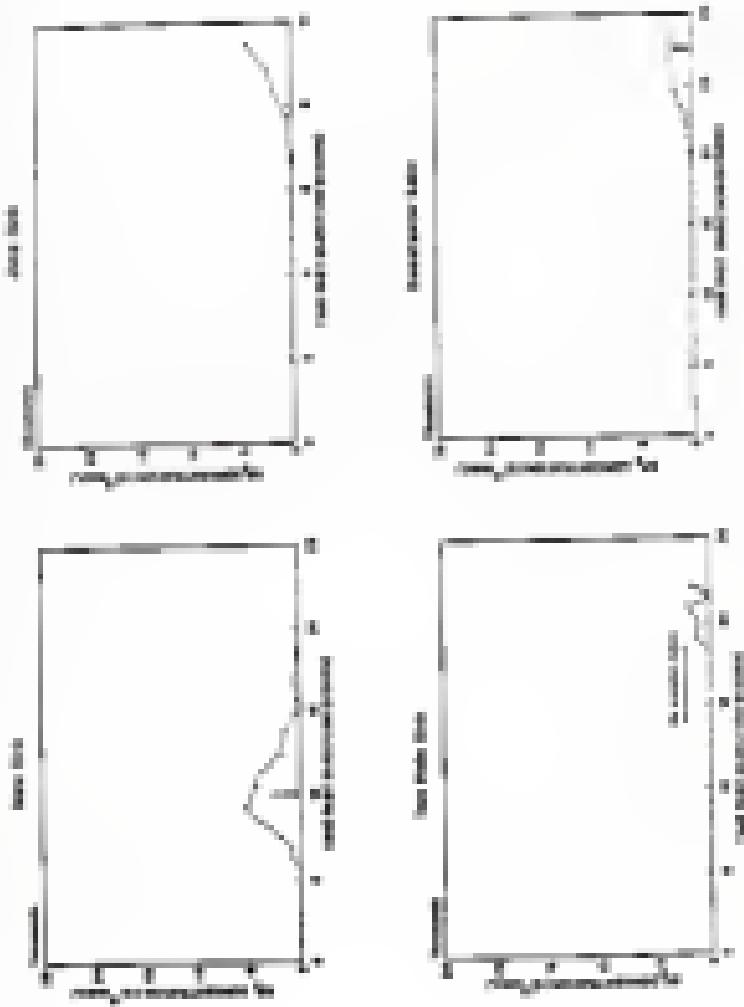


Figure 18. Concentration response curves for four different treatments, T1, T2, T3, and T4, measured over time.

Table 4. Travel times for 10^6 ml minute in O'Leary State Park.

Site	Distance from O'Leary Site (m)	Distance		Passage (ml/yr)	T ₁ (min)	T ₂ (min)	Av. Vel. (ml/yr)
		T ₁ (min)	T ₂ (min)				
O'Leary	0.00	14	121	120	34	34	0.00
Rowine	1.87	181	*	*	*	*	*
TRAILHEAD	11.33	180	10.8	600	480	480	0.00
Small	14.74	288	10.8	424	312	312	0.00
New	14.74	100	10.8	143	312	312	0.00
STATION	17.91	489	*	*	*	*	*
Two Roads	32.07	480	*	*	*	*	*
Interstate	47.61	620	11.67	*	1380	1380	0.00
None	50.01	100	10.8	100			
O'Leary (10^6)	180	18	72	34	72	72	0.00

A period of sampling was too short, \Rightarrow no 10^6 was detected. T_1 = time to leading edge of response, T_2 = time to peak concentration, T = travel time of centroid of the 10^6 area. T_1 , travel times were calculated from the mid-point of the two-hour injection (1 hour), except in the case of the response curve for the 10^6 site, 200 injection, which could only be monitored at O'Leary Park. As distance from the injection site at O'Leary site increases, the top response curve moves due to dispersion starting and the result is a double-traced response curve at Small Park, New Park and Interstate Park. Calculated mean underground flow velocity between O'Leary Park and Interstate Park is 4.3 km/day.

be monitored at Upper Pond. In this case, $\langle V \rangle$ was calculated from the point in time when the ^{37}Ar mixture remaining in the barrel was doped into Orange Creek. Table 4 also provides the average travel velocities associated using the centroid of new travel times and the straight line distance between the sinks. Using these data, an average underground flow velocity of 4.3 km/day between Orange Creek and Sweetwater Lake was determined for July, 1990, a period of unusually high flow (60 m³/s, during July 1990 versus 10 m³/s normal flow and 1980, 1981).

The entire passage of the tracer cloud was recorded at four of the eight sampling locations (Upper Pond, Pomeroy Creek sink, Sweet Creek, and New Creek). Sampling did not occur long enough at Pomeroy Creek nor the three most distant sinks from the injection point (Blue Creek, Two Hole and Sweetwater Lake). During 18 hours of monitoring, ^{37}Ar was not detected at the Santa Fe River River. One possible explanation for not detecting any ^{37}Ar is that the duration of the sampling period required to monitor the tracer was underestimated and sampling was stopped before the leading edge of the ^{37}Ar front arrived at the Santa Fe River River. Another possibility is that the tracer losses caused by ground water, added along the flow path, so that the concentration was to low to detect. Another possibility is that the river sites were not the primary reservoir of the underground Santa Fe River.

A significant decrease of about 50% in ΔF_2 concentration noted between O'Lea's Creek and the River Riss reduced the possibility of tracer dilution by mixing with ground water. Downslope measurements obtained during the experiment, however, did not reduce a gap between a flow of about 4 m^3/s between O'Lea's Creek (11.3 m^3/s) and the River Riss (27.4 m^3/s).

Interbasin Co-Storage in River Riss

Because ΔF_2 was not detected at the River Riss in the first tracing experiment, a subsequent study was carried out between the point of first ΔF_2 detection, reservoir Lake and River Riss. In this experiment ΔF_2 was injected into reservoir Lake in the downflow end of the sink. The injection process was the same as the one used in the O'Lea Creek injection with a two-hour injection period of 300 L of ΔF_2 exhausted, reservoir lake water. A sampling schedule based on equidistant ten and eleven wet days produced four three downflow locations at the River Riss, and 10, 11 and 120 m downstream of the River Riss. In addition, ground water levels and velocities were also estimated based upon the earlier tracing experiment, which further determined when sampling was to begin and end for this experiment.

In this trace, ΔF_2 was detected at River Riss providing evidence of a link between reservoir Lake and River Riss. Since the connection between O'Lea Creek and reservoir Lake

was established in the first tracer, the data from the second tracer confirm that the River Riss is a path of emergence for some portion of the Santa Fe River flow diverted into artesian wells. Yet, we also detected at the locations 10 and 20 a diversion of the River Riss, revealing the possible emergence points of diverted Santa Fe River water.

The tracer response plots for the locations sampled, shown in Figure 204, are not "ideal" smooth response curves such as those associated with the sinkholes monitored in the first tracer study. Instead, they are characterized by multiple peaks indicating the sporadic arrival of the tracer at all three locations. These data suggest that the underground flow of the Santa Fe River between Mountain Lake and the River Riss does not take a singular path, but possibly multiple pathways.

Santa Riss to Santa Fe River wells

As a result of the flow line water tracing experiments, a connection between all the sinks monitored in the park was established. However, beyond Santa Riss it appeared that there was some ground water augmentation or undersaturated Santa Fe River water directed to this complex system. To better establish the relationships between ground water and underground Santa Fe River water downstream of Santa Riss, another water tracing experiment was undertaken. In addition, this tracing experiment provided the opportunity

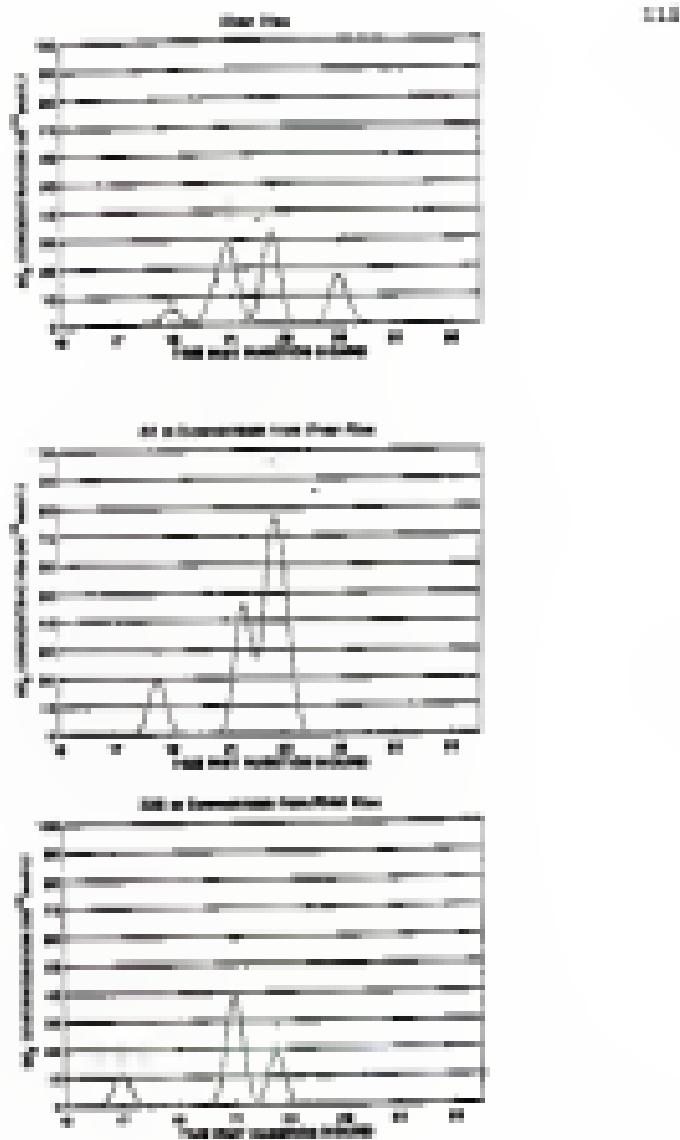


Figure 10. Concentration response curves. See Data file 8 for experimental details.

to compare rhodamine with dye, the most frequently used ground water tracer, and (c), the newly developing ground water tracing technique.

The tracer solution was prepared as described previously and a 100 ml solution of pure rhodamine WT was added to this barrel. The 50₁ and rhodamine WT solution was increased to 1000 ml via type tubing at approximately 1.75-2 l/min. The 500-depth injection of this 50₁/rhodamine solution into the well was continuous over the next two hours. Two hours prior to tracer injection, packets filled with activated charcoal were placed at various sampling points in the 500 ft well. Immediately after the tracer was added to the 500 ft River 200 m downstream of the River site, in order to establish background readings for rhodamine WT. After completing the injection, these packets were collected and replaced. These packets were rinsed with water and stored on ice until their analysis.

Based upon the results of the two earlier tracing trouting experiments, a sampling scheme was established at each of the four locations. 50₁ water samples were collected about every half-hour beginning about 10 min after injection at two sites and ending about 35 hours after injection of the tracer to the lower Santa Fe River. The rhodamine WT packets were changed at about one hour intervals over that same sampling period.

SF_6 was detected at the Hall sink, Southern Lake, the begin of river line, and at the falls 100 meters below the River River. The concentration response curves for these locations are shown in figures 29 and 30. Arrival times for the leading edge of the tracer (T₁), the travel time of the centroid of the SF_6 mass (T₂), and the total tracer passage time are shown in table 7. The average SF_6 travel velocities calculated from the travel times of the centroid of the SF_6 mass and the straight line distance between the sinks are also shown in table 7. Maximum SF_6 dye was also detected at all the sampling sites. These results also are shown in Figures 29 and 31. Values were recorded as "no response", "weak", "moderate", "strong" and "very strong" as only relative values of intensity could be obtained due to the limitations of the analytical equipment. The maximum sample packets were collected at four hour intervals which imposes a delayed peak response curve over that of the SF_6 sample curve. This delay in maximum is in response to the sampling interval, not the travel time of the tracer.

The arrival of the tracer front and the most dispensing peak occurred 30 and 45 minutes later than downstream than at the start of river River. SF_6 detected at the falls possibly represents the same slug of tracer detected at the river's discharge. The quantity of tracer recovered at the falls is 60% of the volume of the tracer recovered at the river, which is a consequence of gas exchange between the

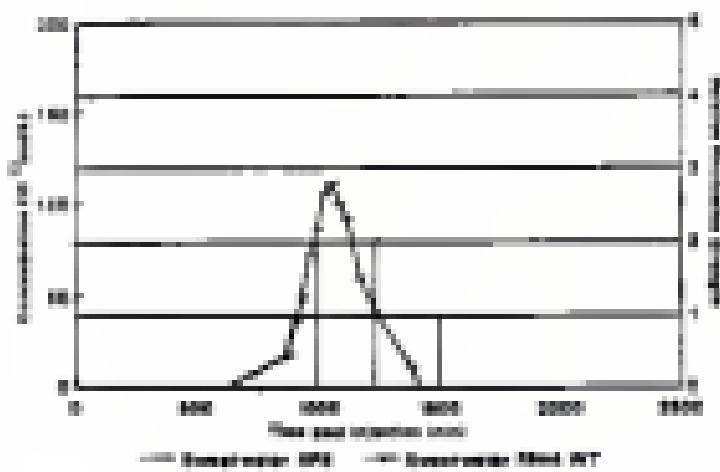
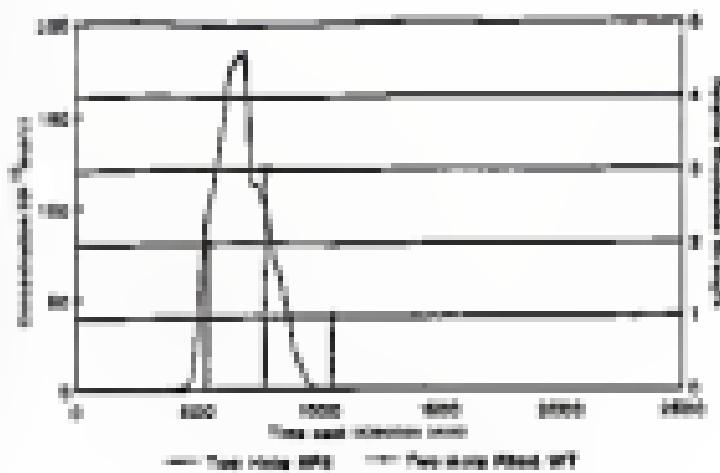


Figure 10. Concentration response curves for Glu-His-Arg.

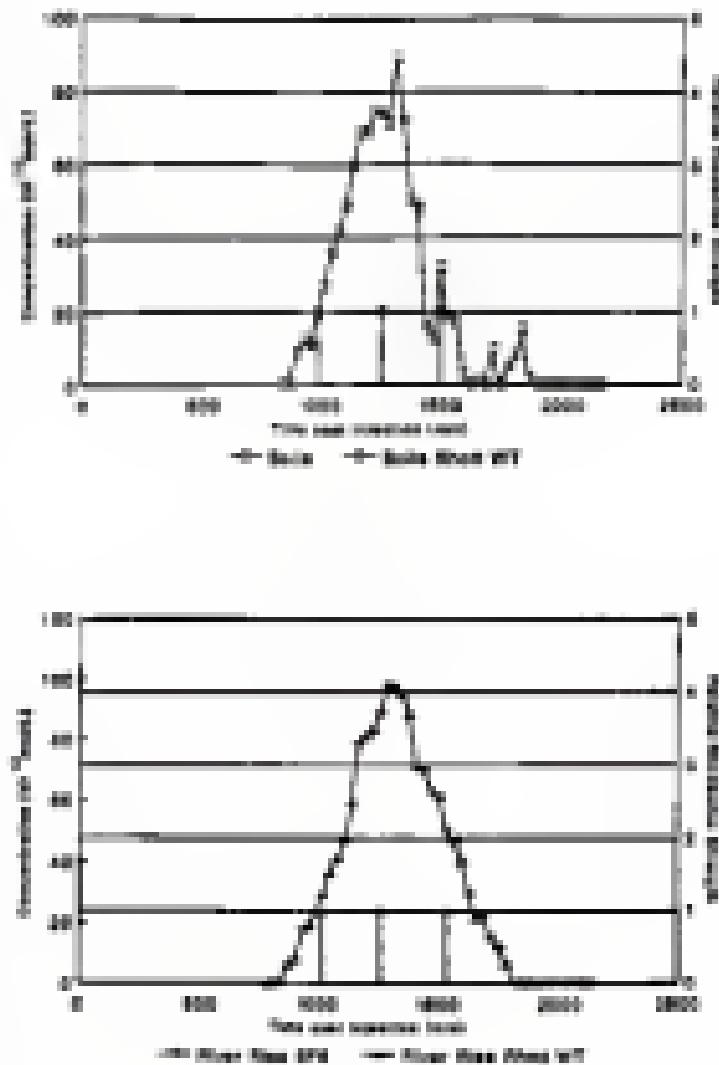


Figure 11. Concentration response curves for Plate B10 experiment.

Table 7. SR₁ travel times for Site's Disk to Santa Fe River River Segment.

Site	Distance between		Permeability	T ₁ (min)	T ₂ (min)	Rate Vel. (m/d)
	Site's Disk	SR ₁				
Two points	1130	300	210	400	300	0.34
Site's Disk	3400	700	1000	800	600	0.34
Santa Fe	6200	870	1400	1500	1200	0.33
ROCK	4500	900	1500	1600	1400	0.33

T₁ = time to leading edge of tracer.

T₂ = travel time of centroid of the SR₁ area.

T₁ travel times were calculated from the midpoint of the two base SR₁ injections (0.3 m/s).

Estimated mean underground flow velocity between Site's Disk and the Santa Fe River Disk is 0.3 m/day.

river and the atmosphere between the two sampling locations. A rough estimate of gas transfer was determined of 0.6 , over the 150 m distance, according to equation 6:

$$0.6 = \frac{0.024 \times 10^{-3} \times 0.0012 \times 10^{-3} \times 150}{0.0012 \times 10^{-3} \times 0.0012 \times 10^{-3}}$$

where:

- k is the gas transfer velocity;
- h is the mean depth (1.3 m);
- v is the stream velocity (0.126 m/s);
- α is the interval under investigation (150 m);
- C_{up} is the discharge at the River Biss (0.01 m³/s);
- C_{bel} is the discharge at the belte (0.1 m³/s);
- C_{up} is the peak concentration of SF_6 at the River Biss (0.6 \times 10⁻³ mol/L); and
- C_{bel} is the peak concentration of SF_6 at the belte (0.1 \times 10⁻³ mol/L).

The calculation yielded a gas transfer coefficient of 27.6 m/s, which is lower than the value of 37.6 m/s obtained in an earlier gas exchange experiment carried out along a 5 m section of the Santa Fe River below the River Biss. At that time stream discharge exceeded 10 m³/s (Villanueva, 1993).

Illustration of the SF_6 concentration response curve at the belte (Figure 12) reveals two additional peaks on the settling line of the response curve, suggesting that some of the instantaneous flow of the Santa Fe River is discharged to the main stem of the river at this point. This finding is supported by discharge measurements obtained during the experiment, which reflect an increase of 0.8 m³/s from 0.6 m³/s at the Santa Fe River Biss to 0.4 m³/s at the belte.

kinetics of the ΔP_2 response curves for each sampling location reveal some interesting points (Figure 39 and 40). The Hole Sink and Sweetwater Lake curves are characterized by a single sharp peak. The curve for the Santa Fe River River, however, is characterized by a sharp rise to a peak and then a more gradual concentration increase to a second peak. This second slope suggests that two partially overlapping response curves are depicted at the Santa Fe River River. At the river, ΔP_2 is downstream, peak separation is more pronounced and two peaks are noticeable in the concentration response curve. Most of the underground river flow surfaces at the river River, but a small flow may be diverted via minor pathways to a discharge point into the river.

Additional support for a two conduit flow route is provided by comparing the total area ΔP_2 measured at each of the sampling sites. If there is equivalent discharge at the Hole Sink, Sweetwater Lake, and the River River, the quantity of ΔP_2 measured is 18.7×10^4 sec. (120×10^3 g), 11.0×10^4 sec. (120×10^3 g), and 10.0×10^4 sec. (120×10^3 g), respectively. Since the area of the basin at the Santa Fe River River is greater than at either site alone, the underground flow of the river must follow more than one flow path. Discharge at the three sampling locations would not be equivalent but does at the Hole Sink and Sweetwater Lake River, if take the area. However,

The estimation of the quantity of tracer recovered at the Lake Sink and Mountain Lake would be too high in such a scenario. The mass of tracer recovered at the Santa Fe River Sink, however, would still be greater than at either the Lake Sink or Mountain Lake. Thus the conclusion that the underground flow of the Santa Fe River follows more than one route between Jim's Sink and the River Sink is still valid.

Summary of Water tracing

The artificial tracer SP, was used successfully in three water tracing investigations in the Santa Fe River basin to track the subsurface pathway of the Santa Fe River between Jim's Sink and the River Sink of the Santa Fe River. The results of the water tracing experiments carried out indicate that the subsurface flow path of the Santa Fe River follows a single primary flow conduit from its origin point at Jim's Sink to River Sink. After Jim's Sink, the underground flow path splits following one conduit at the Lake Sink and then to the Santa Fe River Sink, and a second pathway to Mountain Lake and then the River Sink. The subsurface flow pathway that is tentatively proposed is shown in Figure 13. These data confirm that (1) the Santa Fe River Sink is the primary emergence of the underground flow of the Santa Fe River and (2) suggest that a small portion of the underground river enters the main area of the

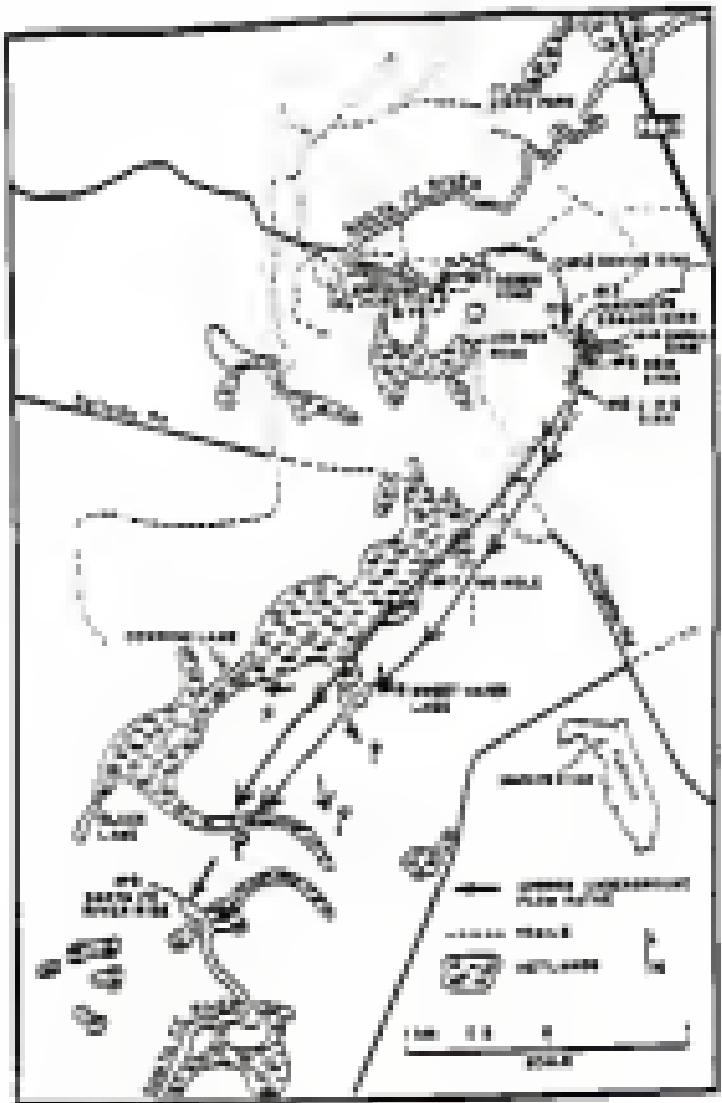


Figure 22. Flow patterns of the underground streams to River through Oltrepo Valsesia Park.

Barita Po River about one m below the River Riau at a spot marked by molls in the river.

Average flow velocities calculated ranged from 1.0 to 3.4 m/day. Such rapid ground water movement renders the water movement of the Barita Po River basin vulnerable to contamination and underscores the urgent need for careful management practices.

The results of this research further confirm that Mn_2 , which is soft, chemically and biologically inert, and capable of being detected in extremely low concentrations, is well suited for water tracing applications in karst terrain. In comparison to fluorescent dye tracers, with its chemical wt. wt. has the advantages of detectability at low concentrations and none of the hydrodynamic problems associated with organic acids, dissolved particulates, and organic material that are associated with fluorescent dyes. This is particularly helpful in hydrologic settings such as the Barita Po River with high organic acid concentrations.

Mn_2 is a volatile compound as the manganese occurs when ground water is exposed to the atmosphere in karst windows. In hydrologic settings where there is no contact between ground water and the atmosphere, however, Mn_2 may have potential as a quantitative tracer. Mn_2 may also have value in determining whether a hydrologic flow network is completely developed in the vadose zone or in a partially flooded vadose zone, as in conditions the zone is either dry or damp.

gradient systems. Further research is needed to properly evaluate the performance of NO_2 in comparison to other proven tracers and to develop additional hydrologic applications for this compound.

Flow-Dominated Analysis

After the completion of the tracing experiments within Okefenokee State Park it appeared that the downstream flow path of the Suwannee River had been characterized. However, the relationship with the ground water along the course had remained unascertained. In order to further establish the link between the two sources of water in the park several flow component analysis experiments were completed. The experiments used both relatively simple techniques and more elaborate techniques such as water temperature gatings and core drilling/stacked techniques such as ^{36}Ar , ^{37}Ar , and major cation concentration analysis. These techniques were employed because of their relative ease of use and their potential to separate or indicate different water types.

Water-Flow Tracer

Water sample sets taken from 18 different water filled fissures throughout the park and from the park's main efflux stream which traps the Floridan Aquifer in the region (Figure 10; Dale Hendrick, personal communication, 1992). Samples were drawn into graduated cylinders as previously described

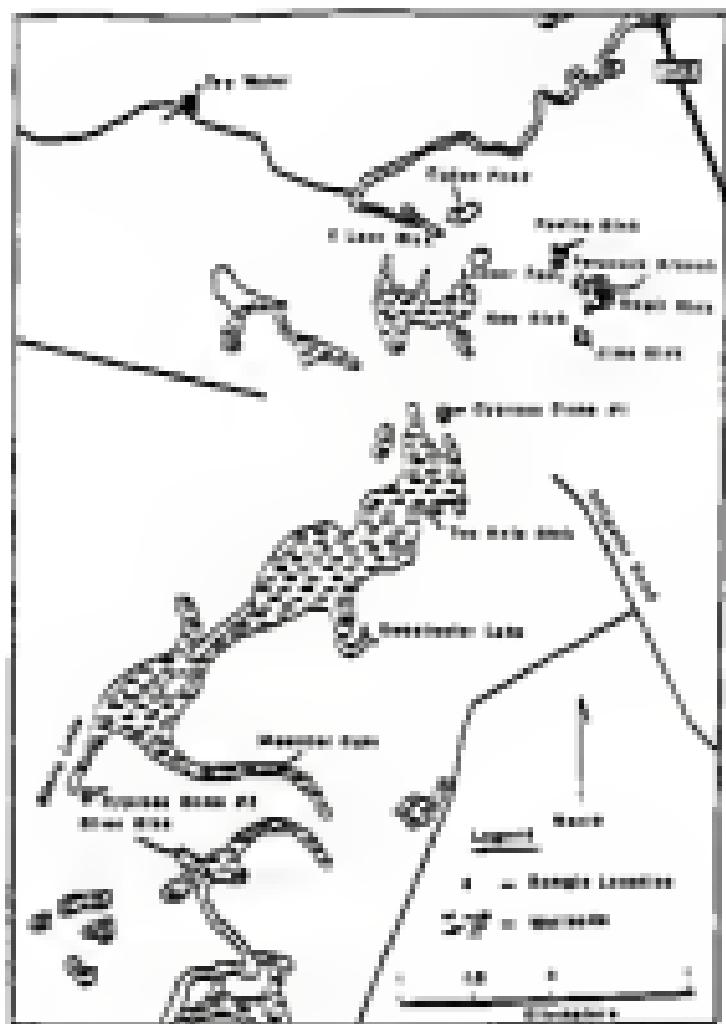


Figure 22. Sample locations for ^{230}Th , ^{226}Ra , major cations and temperature.

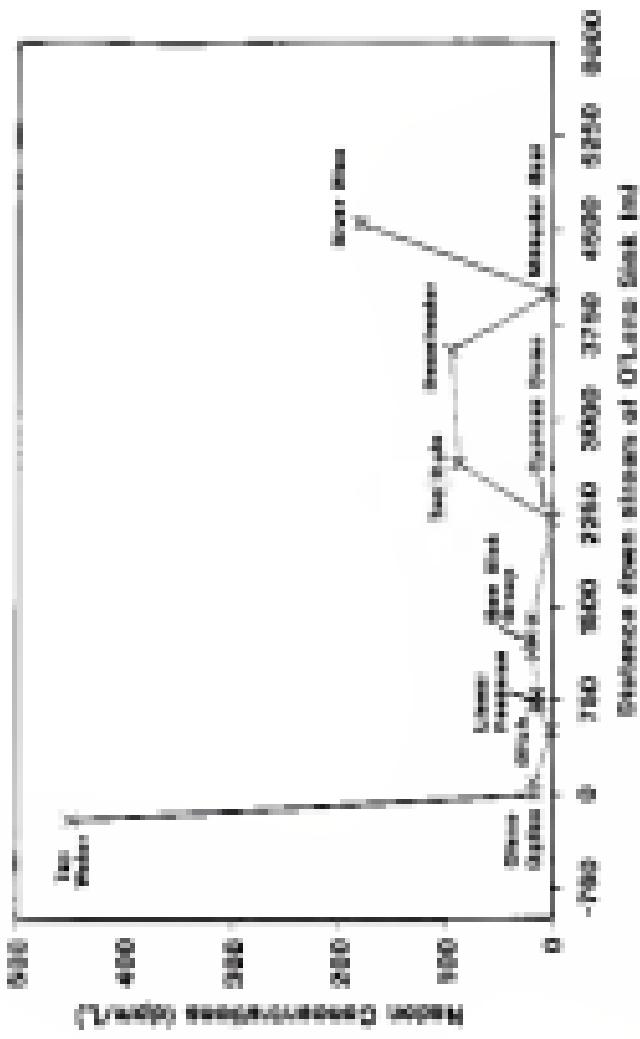


Figure 12. Hatched-EDS concentrations for hatched polymer. (continued)

and analysed as before (see Materials and Methods chapter 3 and Figure 17).

The results of this research show the ^{226}Ra levels at each location (Figure 34). The top water sample in this research reflects that of typical ground water conditions in the area (B132a, personal communication, 1992). The ^{226}Ra concentrations found throughout the park in the surface section (eg. Shire Head, River Wadsworth features, the sink group including Shire Head) are essentially equivalent to atmospheric background levels. However, beyond Shire Head (eg. The Vale, Batherwold Lake and River Wye) the ^{226}Ra levels steadily increase towards the ground water levels.

This increase in radon levels suggests an influx of ground water into these sinks along the alluvium pack of the River Wye. The surface features, (opposite dam and smaller sink, having low ^{226}Ra levels, sometimes of Shire Head) also confirm that the surface water is not directly, hydrologically connected to the ground water in this region of the park.

3.6. Research

The water samples were collected from 27 different water filled features located throughout Orton State Park (Figure 35). Each sample was collected at a depth of about 1.0 m where possible. Samples were collected and analysed

as previously described. In theory, the oxygen isotopic value for the ground water and the surface water should be different because of the evaporative and precipitation effects on the composition of the surface water. The ground water value will have a characteristic signature value based primarily upon the source of the ground water and any mixing the water has had with other ground water. The surface water on the other hand will have a signature value based primarily upon the $\delta^{18}\text{O}$ value of the precipitation, and any subsequent or previous rain events and the evaporative effects on the surface water body. The surface water, if it has undergone substantial evaporation will relinquish the lighter isotopic $\delta^{18}\text{O}$ to the atmosphere leaving the residual water heavier or more enriched in $\delta^{18}\text{O}$ (Fritz, 1980). The process causes the $\delta^{18}\text{O}$ value to increase relative to standard mean ocean water values (SMOW). Because this water has remained at the surface and has not been mixed with either pure ground water or with new precipitation it can easily be distinguished from ground water.

Figure 18 shows the $\delta^{18}\text{O}$ values for the water bodies sampled in O'Leary State Park. In this figure there are three distinct groups of water. The first group appears to be pure ground water and is represented by the top series, which is close to the Florida depleted. The second group is surface water and is represented by the upper data, scattered near and to some degree the drainage divide. The

third group is a mixture of the surface water and the ground water and is represented by essentially all other features labelled on the figure.

These results suggest that there are three different types of water within State Park and that there is a contribution of ground water to the underground flows in surface water beyond the surface lake.

cation concentrations

Total cation concentrations as well as cation ratios were evaluated. Al^{3+} , Ca^{2+} , Mg^{2+} , K^+ , and Na^+ were detected at all 21, 22 locations (Figure 10). Of these, Ca^{2+} appears to be the element that best separates ground water and surface water samples. All other cations appear to give inconsistent results. Several cation ratios were also evaluated in order to separate water types (Table 8). According to Tischler (1980) ratios of Mg/Ca , Na/K and $(\text{Ca}+\text{Mg})/(\text{Na}+\text{K})$ have been used to establish water proportions. Mg/Ca ratios of 0.5-0.7 indicate a limestone source, 0.7-0.9 ratios indicate dolomite and ratios with indicate a silicate source rock (Fetter, 1980; Fetter, 1990). Na/K ratios equal to 1.0 indicate meteoric and those between 1.8 and 2.0 indicate water that is close to the recharge area. In addition, $(\text{Ca}+\text{Mg})/(\text{Na}+\text{K})$ ratios greater than 1.0 also indicate that water is close to the recharge area. The Na/K ratio and $(\text{Ca}+\text{Mg})/(\text{Na}+\text{K})$ ratio

Figure 15. The relative peak heights of the different isomers of the monosubstituted benzene isomers with respect to the relative peak height of the unsubstituted benzene isomer.

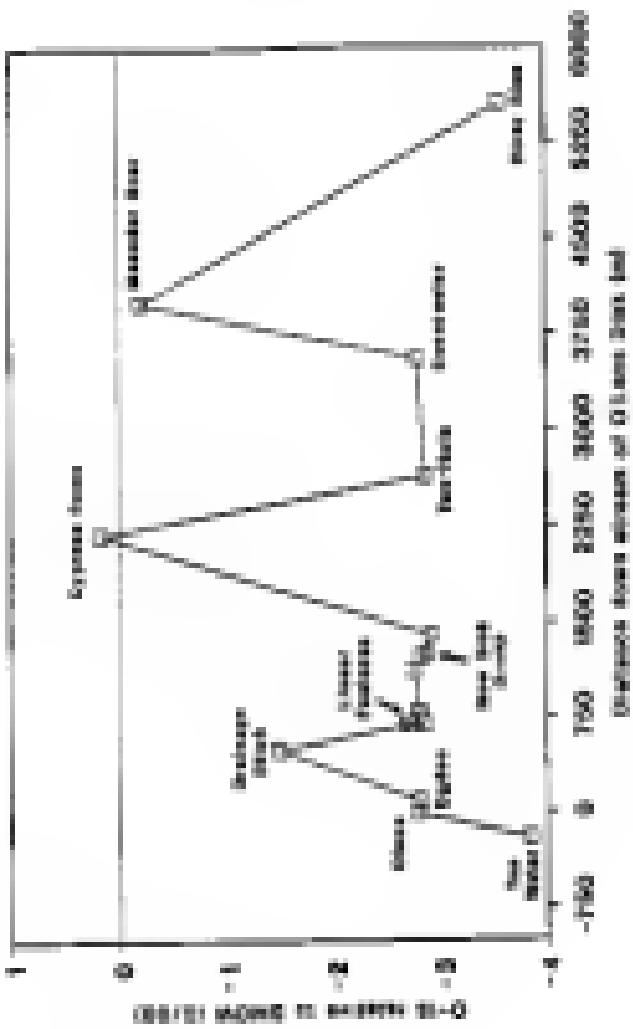


Table 4. Saline ratios for locations throughout O'Loughlin State Park.

Location	mg/L Mg/Ca	mg/L Mg/Na	mg/L (Mg+Na)/ (Mg+Na)
Top Vertic	0.000	0.0-0.00	100-100
4' Game Sink	1.000	1.0-1.00	0.2-0.7
Drainage ditch	1.417	1.4-1.70	0.200
Opales Pond	1.178	1.1-1.80	0.200
Bottom Sink	0.994	1.1-1.90	0.2-0.7
Linear Feature #1	0.793	0.6-0.90	0.2-0.6
Linear Feature #2	0.698	0.4-0.90	0.2-0.7
Linear Feature #3	0.794	0.6-0.90	0.2-0.7
Reeders Ranch	0.888	0.6-0.90	0.2-0.6
Small Sink	1.017	1.1-1.90	0.2-0.7
Big Sink	1.094	1.1-1.90	0.2-0.7
Stone Sink	0.843	0.4-0.90	0.2-0.6
Cypress Dome #1	0.344	0.1-0.70	0.1-0.6
Two Hole Sink	0.470	0.2-0.90	0.1-0.7
Reeders Ranch #1	1.018	0.6-1.90	0.2-0.6
Black Lake	0.770	0.6-0.90	0.2-0.6
Cypress Dome #2	0.890	0.6-0.90	0.2-0.6
Swallowing Lake	0.807	0.6-0.90	0.2-0.6
River Sinks	0.499	0.1-0.70	0.1-0.6
River Sinks + 30m	0.215	0.1-0.40	0.1-0.4
River Sinks + 200m	0.137	0.1-0.20	0.1-0.2
Precipitation	0.000	0.0-0.0	0.0-0.0
Average	0.835	0.5-0.70	0.2-0.7
Std. Dev.	0.403	0.2-0.60	0.1-0.7

Mg/Ca = 0.8 - 0.7, Limestone

Mg/Na = 0.7 - 0.4, dolomitic

Mg/Na = 0-0.5, dolomite

Mg/Na = 0.7, dolomitic

Mg/Na = 0.0, dolomitic

Mg/Na = 0-0.1, where no dol. noted

(Ca+Mg)/(Mg+Na) = 0-1.0, near recharge

(positive from Petrone, 1990)

plotted varying Mg/Ca ratios with no apparent trends or correlations.

Using the Mg/Ca ratio, ground water and surface water groupings of water bodies can be delineated. Those features having a ratio of greater than one reflect the water chemistry of surface water bodies. These include: River Sink, drainage ditch, Cypress Pond, Rock Sink, and the number four. Those features having a Mg/Ca ratio of less than one reflect a ground water influenced feature. These features include: top water, Three Features 1, 2, and 3, the Blue Sink and the River Sink sampling locations.

Ground water sites reveal distinct types of water groups (Weller, 1938; Rose, 1962). When plotted, the cation concentrations of Mg^{2+} , Ca^{2+} and $\text{Na}^{+}/\text{K}^{+}$ show three distinct types of water, calcium dominated type, a sodium or potassium type and a non-dominated ion type which constitutes the largest number of samples in this area (Figure 34). Those features that are dominated by the calcium ions are the domesites features: the Blue Sink, Black Lake, Cypress Pond #1 and the upgradient top water site that was taken from the upper basin of the park's northern entrance. The non-dominant ion features include the three River Features, the three River Sinks samples, and the upgradient sites (plastic sink, Sweetwater Lake, Blue Sink, rock sink, Paradise Ranch sink). The sodium and potassium dominated features primarily

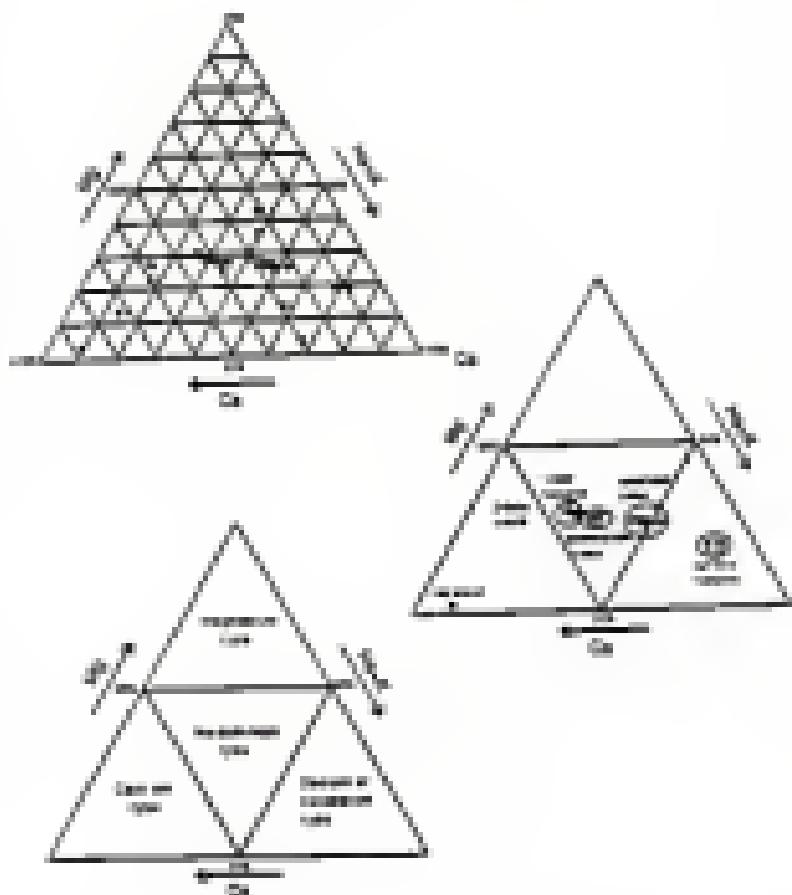


Figure 10. Calcium concentrations at soil horizons throughout a boreal forest (top), percentage of selected textures through the peat (middle) and mineral soil (bottom) ice spaces within ternary diagrams (bottom, after Pettersson and Kett, 1999).

include the variated features, such as the number acres and the drainage divides.

The middle diagram in figure 34 reveals a trend of increasing $\delta^{18}\text{O}$ (ground water) influence with increasing distance through the park. The surficial features represent the surface and under water type and the top water sample represents the ground water and water. The upstream sites, those above the 's' link, may closely resemble the chemical signature of the surface water in the area. The downstream sites, mostly wastewater sites and the three river sites (sections) more closely resemble the chemical signature of the ground water (top water sample). The Lower Section which lie within 100s of River Link were closely resemble the action of the ground water as well.

Temperature Transect

In a previous study, Shervin (1982) reported that it was possible to detect ground water in all the sites monitored in this study during a period when Barts To River discharge to O'lees River Park was temporary, but completely dried due to evaporation in the upper reaches of the Barts To River. To determine the extent that the underground Barts To River flow is impacted by ground water, temperature measurements were utilized to calculate the relative proportion of ground water found in three sites hydrologically connected to the underground pathway all

the Santa Fe River. Five additional water-filled marsh basins in O'Leno State Park were also monitored for temperature gradients.

The first set of 13 water temperature measurements was taken on January 13, 1982. The air temperature was 11°C and the water in O'Leno Sink was 10°C. Ground water was measured to be 10°C (Journal and notes, 1982; Florida Geological Survey, 1982). The temperature measurements revealed that those areas in hydrologic contact with the underground flow of the Santa Fe River between O'Leno Pond and Jim's Sink were warmer than the Santa Fe River by about 0.5°C, supporting the ground water mixing with the underground flow of the Santa Fe River (Figure 37). The most significant increase in water temperature, however, occurred at the Rock Sink. The water temperature in the Rock Sink was 3.5°C greater than the previous sink measured, Jim's Sink. Black Lake was measured because it had a maximum depth of only three meters making it a significant feature not in hydrologic contact with the underground flow of the Santa Fe River. Black Lake recorded a temperature much lower than ground water, 14°C.

The additional temperature readings were taken on January 14 and March 24, 1982. The ambient air temperature was 19°C, however, as the temperature gradients were dissipated and the results, although similar, are less drastic. On January 14, a significant averaging of temperatures may have taken place due to a previous night's

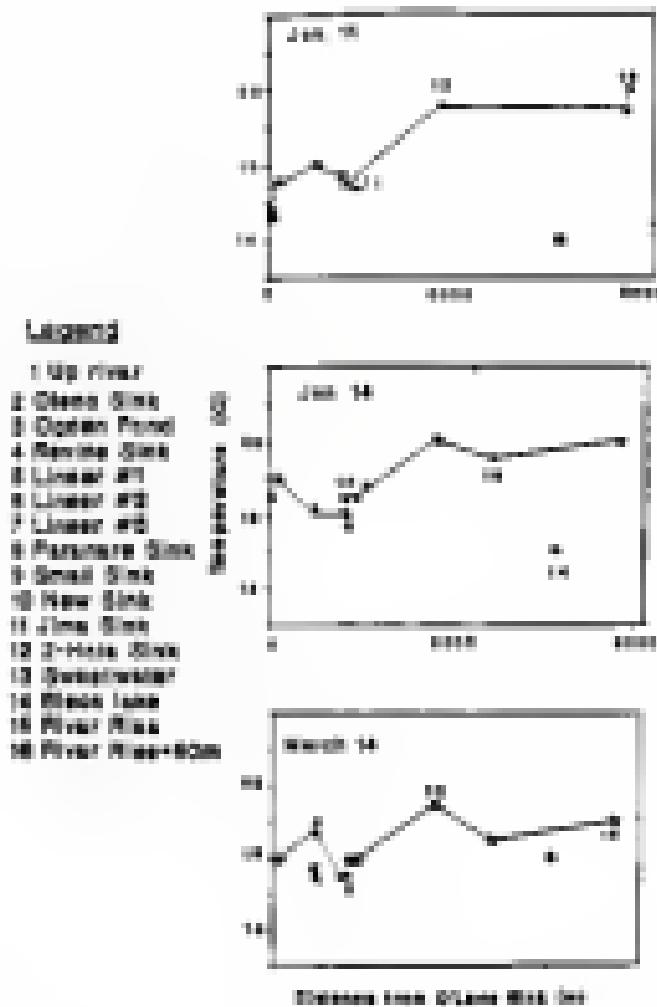


Figure 17. Suspended readings taken from the 1990 Census of the state park.

mined in the area of cut as ground conduction, (see Headrick, 1982).

Because the Santa Fe River follows a subterranean flow path for at least 21 kilometers before emerging at the River Mine, one factor to attribute to mixing with warmer ground water may result in elevated temperatures. These include the type of flow, the surface area of the underground water in contact with the walls of the conduit, and exposure of ground water to the atmosphere. The least important of these is the transfer of heat from the limestone aquifer to the underground stream across the rock/water boundary. This is because limestone has a very low heat conductivity (0.0001 gram calories per centimeter degree second, Pinner and Bergart, 1933; Detwiler, 1949; Juster and Sebastian, 1991). In fact, rocks add the groundwater little heat to the ground water system (Lohmeyer, 1982).

Assuming that the mixing could not have been achieved by contact with the limestone aquifer, and a relatively short time period which ground water is exposed to the atmosphere (about 40 hours), it is suggested that mixing of surface water with warmer ground water offers the best explanation for the increased temperatures observed. Calculations of ratios in percent between ground water and Santa Fe River water measured at each sink can be accomplished by ensuring that the measured temperatures of

0°C less sink (18°C) and River Kise (12°C) are respectively the minimum and maximum temperatures attainable by the water in this region. therefore, a one degree increase in the measured sink water temperature would be equal to about a 15% contribution of ground water. For example, at River sink, the temperature increase of 3°C to 18°C represents a 15% ground water influx to the underground sink of the main Po River. Based on the temperature measurements, this ratio of about 45/40 or 45/35 (ground water/underground water) in River water remains fairly uniform through River sink, a distance of 1.5 km. At the River sink, however, the water temperature drops 4°C from 12°C at Orme sink to 8°C, supporting the ground water explanation. The water temperature at the River Kise is 12°C, which is the same as local ground water temperature. This finding suggests that there is no significant influx Po River water into at this point and that it has dispersed or sustained elsewhere in its underground path. However, this can not be true because the 27, 1991, sampling specimens revealed ammonium counts of 37, at the River Kise, and demonstrated a hydraulic connection between Orme sink and the River Kise. Temperature measurements confirm that River sink, which receives water from the other downstream sinks, is only a euryhaline feature with no ground water or Po River water component. This finding is corroborated by the fact that the median depth is only three meters (Gidviri, 1992).

Computer Modelling

Computer modelling of an aquifer requires making several assumptions about aquifer parameters. These assumptions include: isotropic conductivities, constant head or no-flow (no boundary), relatively homogeneous aquifer material, and variable ranges of hydraulic conductivity values (say, 0.01 to 500).

Various scenarios were attempted to model the area based on the water flow velocities estimated from the tracing experiments. Because of the anisotropic conditions that exist and the complex interactions between ground and surface water the area, it was impossible to model with the current software packages available.

The initial model setup shows the distribution of the discretized area, boundary conditions, water table elevation and surface water features (Figure 18). This model set up was completed using *seawater*[®] (Doherty and Miller, 1990) a computer aided design software package for ground water modelling. Because there is no confined layer in the modelled area a two-dimensional model setup was produced. A three-dimensional model is normally setup when two or more aquifers are found within a specific area. This pre-processed input file was then sent to the main computer program *mod*[®] (method of characteristics, Rendell and Wedderburn, 1991) for interpretation.

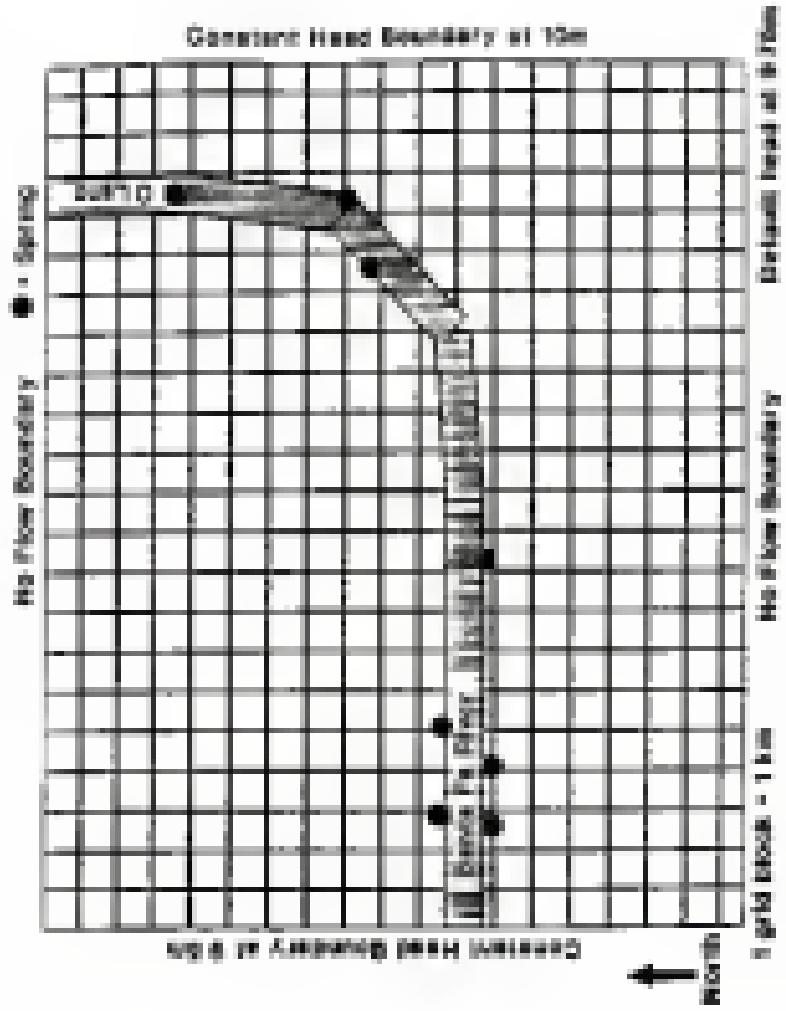


Figure 3.1. Schematic model with one (the standard) and two (the robust) players.

In theory the constant head boundaries at the western and eastern edge of the mapped area act as the driving forces of water flow. A default head elevation is assigned to all other gridded areas and the computer then calculates the potential head values over a certain time interval based upon the aquifer's physical properties (thickness, hydraulic conductivity, storativity, leakage, recharge). In most non-aqueous aquifer settings this process is relatively straightforward.

In this karstic region hydraulic conductivities of the aquifer may vary by several orders of magnitude within the same aquifer (see see Beck, 1991). However, these trends in conductivities form no obvious geological or topographic boundaries. To further complicate this karstic setting, numerous springs are located in the area which creates another modeling challenge. This challenge is created because the computer model does not have a "spring" parameter which allows for the accurate depiction of a spring in the model. Instead, the springs were modeled as pumping wells to the river with their recharge values equivalent to each spring's output. The river, however, as previously noted, is directly connected to the underlying aquifer and is sending any discharge with the top of the potentiometric surface of the Floridan Aquifer.

Because of the complexity of the model and the abnormally high hydraulic conductivities the computer

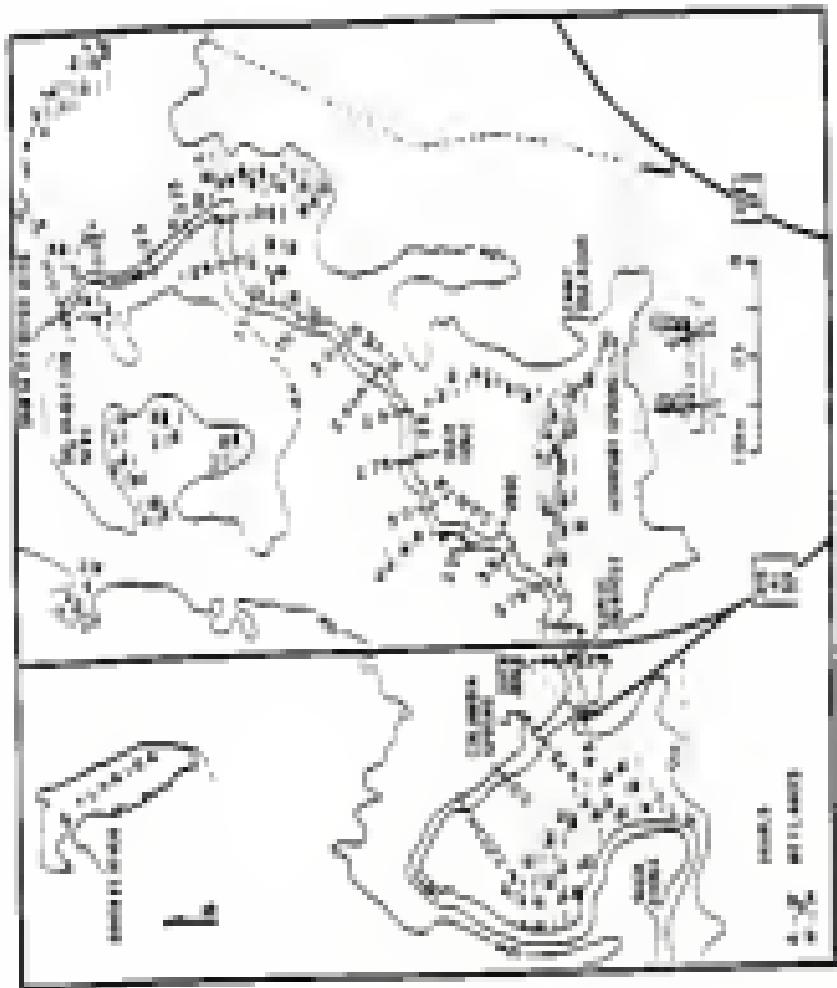
progress was unable to process the data. The progress failed for several reasons. The reasons include first, the computer program has a hydraulic mass balance option that allows for only a 10% error in the amount of water going into and exiting from the aquifer. The abnormally high conductivities of the aquifer and the numerous springs rising the stream caused a gross imbalance in the water exiting the aquifer. Second, the recharging wells to the surface effectively lowered the ground water levels to unrealistic levels. These unrealistic levels caused "pounds" of water representing each spring. Third, because surface water and ground water are one in the case in many cases, they can not be quantitatively described and accounted for in the model. This third problem again results near-saturated aquifer in the model. Fourth, the hydrologic conditions of the aquifer were not reproducible in computer solution format because of the general lack of knowledge of the three dimensional location of conduct patterns surrounding the Roubia River. This fourth problem lead to an unrealistic homogeneous aquifer setting.

numerous attempts were made to adjust the model to produce more output, however all were unsuccessful. It is now understood that even with all the data collected from this report and many others, the area in many ways is still perplexing. These results are corroborated by several authors that have suggested that no current ground water

computer model can accurately characterize karstic conditions (Dunn Qualls, personal communication, 2004; Paul Lepous, personal communication, 2004).

Sampling Results

Sampling locations along the Santa Fe River for the first experiment are shown in figure 10. Figure 10 shows the ${}^{87}\text{Sr}$, ${}^{88}\text{Sr}$ and stream-flow profiles for this reach. Berrnsy springs is the only documented major contributor of ground water to the Santa Fe River along this reach. However, distinct peaks in the ${}^{88}\text{Sr}$ profile reveal injections of unsewered ground water inflow. The stream-flow data indicates that the Santa Fe River flow is increased by as much as 1.1 m^3/s upstream of Berrnsy springs. ${}^{87}\text{Sr}$ concentrations decline downstream of the injection point due to gas exchange, while increases in the ${}^{88}\text{Sr}$ concentrations are noted except at 3.75 km and 4.0 km (Berrnsy springs). The increase in ${}^{88}\text{Sr}$ concentrations may reflect downgradient mixing in the stream or the return flow previously diverted from the main stream channel to conduits in the limestone aquifer further upstream. At 3.75 km and 4.15 km, the large hydraulic head stream flow is diverted underground are clearly visible. Stream water lost to sub-channel conduit flow results in no change in tracer concentrations in the stream at the point of flow loss. Downstream of the flow loss point, ${}^{87}\text{Sr}$ concentrations continue to decline in



Geographia
1960
Geographia
1960
Geographia
1960
Geographia
1960

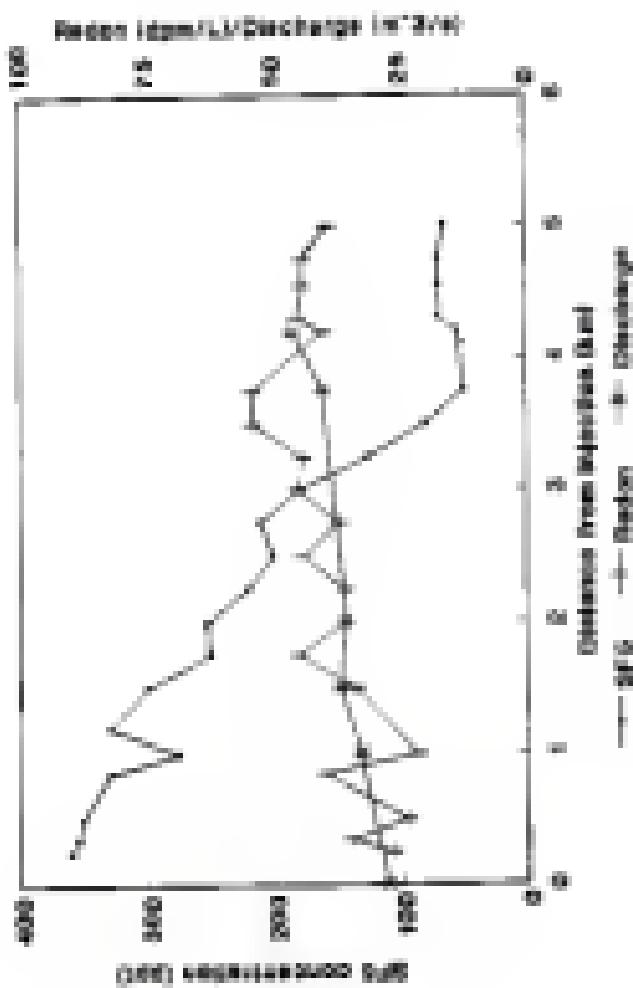
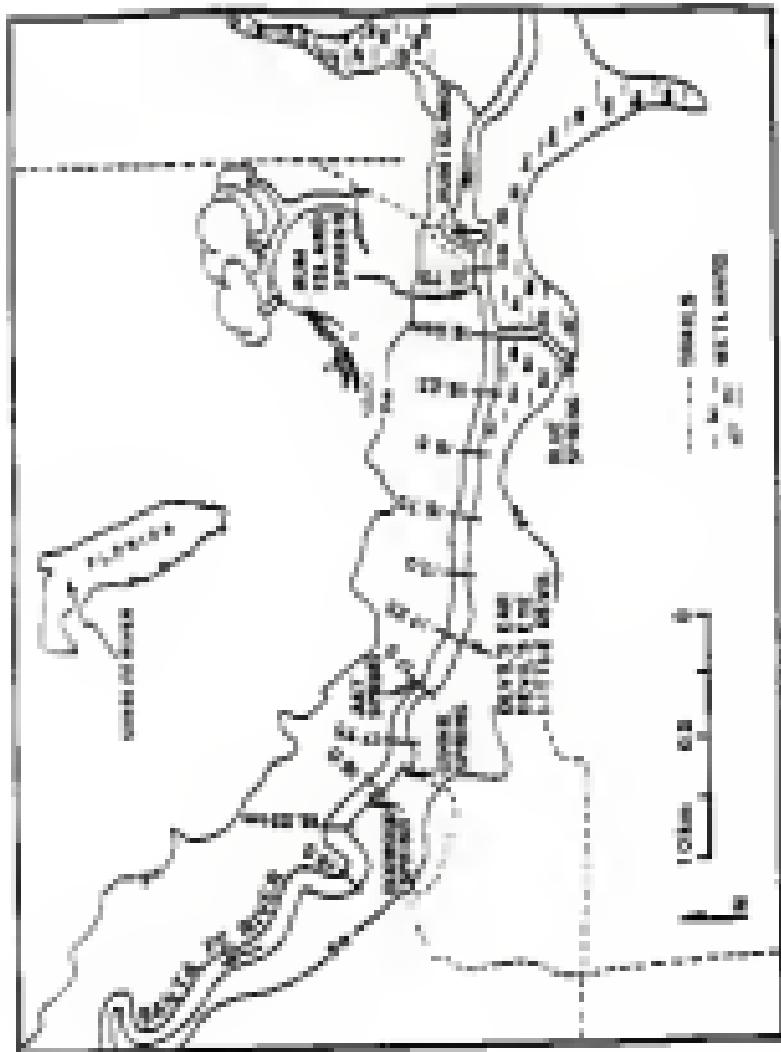


Figure 4: Redden concentrations and stream discharge from two dates in 1997, measured at the same sampling locations.

the stream-flow due to gas exchange.

$\delta^4\text{He}$ is the stream-flow diluted underground, however, is removed from the atmosphere's content and gas exchange no longer occurs. $\delta^4\text{He}$ concentrations therefore remain the same in the underground flow, except where dilution due to mixing with ground water takes place. The influx of stream flow of previous surface water to the Santa Fe River is indicated by $\delta^4\text{He}$ concentrations that are higher than concentrations in samples collected in the river upstream, which will have a decline due to gas exchange. Catuccia Spring discharges to the Santa Fe River and represents the return of stream flow from underground by means of a seep in the Santa Fe River at 4.10 to be shown by elevated $\delta^4\text{He}$ concentrations at 4.10 km.

Sampling locations for the second reseepion experiment are shown in figure 41 and the $\delta^4\text{He}$, ^{226}Ra and stream flow profiles are shown in figure 42. Both types of $\delta^4\text{He}$ profiles are shown in order to represent the integrated and year sampling results. A number of springs add to stream flow along this reach of the Santa Fe River. The ^{226}Ra peaks in figure 42 match the locations of known springs. Unlike the first reseepion experiment, $\delta^4\text{He}$ concentrations do not decline as expected (figure 42). The $\delta^4\text{He}$ profiles are instead characterized by many spikes possibly caused by pumping of ground water with stream flow. Some sections of the $\delta^4\text{He}$ peaks, however, closely correspond with the ^{226}Ra



THE 1970 CENSUS OF POPULATION: THE 1970 CENSUS OF POPULATION

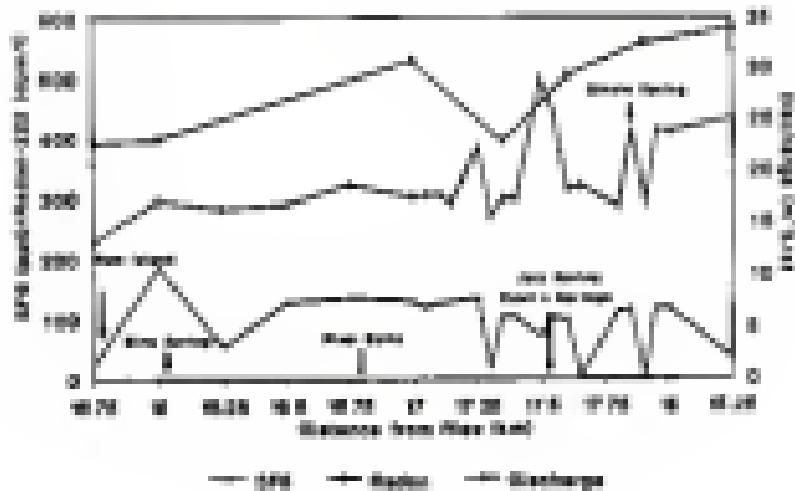


Figure 13. Multiple borehole and video profiles for the first saturation experiment.

gauge and three springs. For example, the ^{37}Ar peak at 17.00 m matches the ^{37}Ar peak that represents ground water discharge from the Devil's Bar, Devil's Eye and Little Devil springs. Another ^{37}Ar peak centered around 17.00 m corresponds to Devil's Eye.

The occurrence of ^{37}Ar and ^{38}Ar concentrations together supports that discharge from the Devil's Bar, Devil's Eye, Little Devil and Devil's Springs is not pure ground water, but a mixture of ground water and water in River water, which was diverted underground at Jamboree spring. Work completed by Kinsowid (1994) supports this theory. Although there is no direct evidence of seepage in the Santa Fe River along this reach, the stream flow profile indicated flow between 17.00 m and 27.75 m (Figure 42). As previously mentioned, the Devil's Bar Cave system, extends beneath the Santa Fe River along the second resevation experiment, Devil's springs, including Devil's Eye, Little Devil and Devil's Bar are physically connected by a network of conduits to the cave system (Kinsowid, 1994). Cave divers have reported intrusions of Devil's Eye water from the Santa Fe River to the Devil's Bar cave. The observations coupled with the ^{37}Ar and ^{38}Ar data provide evidence of the influence of the Devil's Bar cave system of interactions between ground water and stream flow in this part of the Santa Fe River (Kinsowid, 1994). A more detailed description of the resevation coefficients calculated and the relationship

between the Santa Fe River and ground water along this stretch of river is discussed in detail (1994).

Gas Transfer

The gas transfer velocity (k) for CH_4 during plume concentrations for each continuous injection was determined according to equation 4. Ground water inflow along the study reaches increased streamflow and diluted the tracer. In addition, there is discharge from various springs to the Santa Fe River. Naturally occurring ^{37}Ar was used to locate of ground water delivery along each reach. Adjusted streamflow values, based on the stream gaging effort, accounted for the dilution by ground water in calculating the gas transfer velocities using ^{37}Ar . Table 5 provides the stream gaging data for the Santa Fe River.

The gas transfer velocity of 82.6 m^2/yr was calculated for the River River reaches upstream between 0.40 km and 3.55 km. This length of reach was used to avoid possible scaling problems at the beginning of the reach and the influence of returning CH_4 -labeled stream flow at Columbia Springs.

The DART/USGS data system shows a consistency difference over time between ground water and stream flow along the Santa Fe River based on the ^{37}Ar and CH_4 data. Also, in this region of study the spring discharge should be regarded as a dynamic mixture of ground water and

Table 3. Stream gauging data for the Santa Fe River, First Reservation Experiment, Silver Creek

Distance from River River (km)	Discharge (m ³ /s)	Depth (m)	Velocity (m/s)
0.00	27.4	1.20	0.145
1.0	27.4	1.20	0.144
2.0	28.6	1.40	0.175
3.0	43.0	1.60	0.245
3.75	62.2	2.00	0.327
4.125	47.4	1.84	0.273

Second Reservation Experiment, Run related to stream spacing

Distance from River River (km)	Discharge(m ³ /s)	Depth(m)	Velocity(m/s)
13.75	22.0	1.20	0.200
13.88	22.0	1.20	0.200
13.98	22.0	1.20	0.200
14.12	22.0	1.20	0.200
14.25	22.0	1.20	0.200
14.38	22.0	1.20	0.200
14.50	22.0	1.20	0.200

Barbe Te River water rather than pure ground water (Klauda, 1994). Because this study involves unconfined intersections of surface and ground water it was not possible to determine the extent to which stream flow altered conductivity of the Devil's Bar Creek nor be necessarily address the quantity of pure ground water discharge along the reach. In an accompanying study by Klauda (1994) a more detailed investigation of the chemistry and gas exchange values for this reach of river was completed. His work revealed an average K_1 value of 4.08 m^2/d and an average K_2 value of 2.39 day^{-1} for this reach of river.

Corrected discharge values (shown in Table 3) were used in the gas exchange calculations in an attempt to take into account stream flow loss and the degree to which tracer concentrations are decreased by dilution resulting from ground water seepage. This method produced gas transfer velocities of 0.013 and 1.9 m^2/d for the deionized and groundwater K_1 data, respectively. These negative values suggest that gas exchange is negligible along this short reach and that the decline in concentrations observed is due entirely to dilution by ground water. Based on the measured stream flow values for the reach gas exchange calculations do not adequately account for dilution by ground water and thus over estimate the value of K_1 . On the other hand, the adjusted stream flow values do not account for the mixing of Barbe Te River water

with pure ground water in the river's bed core and the subsequent discharge of some mixture of the two water types along the reach.

Tables 10 and 11 show the calculated values of K_{10} and K_{11} for intervals between the stream gauging stations in the Santa Fe River. As previously mentioned, comparison of K values between stream segments underscores the degree of variability induced by the non-uniformity of the stream channel and incomplete mixing of ground water with stream flow.

Although ^{226}Ra was used to estimate gas exchange in the river, no attempt was made in the 1982 stream reach of the Santa Fe River because of the close proximity and great number of ground water inflows to the Santa Fe River. These factors made it impossible to determine the rate of gas exchange between pulses of ^{226}Ra in the stream. The interested reader is referred to Kinsold (1984) for a more detailed discussion of methods involved in estimating gas exchange in this portion of the Santa Fe River.

Respiration coefficients

Santa Fe River gas transfer velocities determined using O_2 were related to the rate of oxygen uptake and expressed as respiration coefficients (R). Temperature strongly controls the gas transfer coefficient determined for these gaseous species used in the stream respiration studies. The

Table 10. Values of δ in meters per day for intervals between the stream gauging locations in the first reservoir experiment.

Stations	Distances		Discharge (m ³ /s)	δ (m/day)	Transit Time for δ (h/s)
	Downstream	Upstream			
1	0.20		27.42	369	
2	1.00	0.20	26.43	377	35.3
3a	0.99	1.00	34.45	368	3.5
3b	0.7	0.48	48.33	496	33.3

Table 11. Values of K in meters per day for intervals between the stream gauge locations in the first discharge experiment.

ID#	Distance from beginning (km)	Diss.	Depth (m)	Mf (gpm/ft)	Transient Velocity (m/d)	
					max. [481] ^a	int. [300]
1	0.15		25.4		1000 [1100]	
4	3.35	3.28	26.7	821 [782]	0.5 [0.3]	
13	3.48	0.38	23.8 [22.3]	899 [782]	1.7 [1.6]	
17	3.58	0.38	23.8 [22.3]	873 [889 - 88.8] 22.8		
21	3.13	0.38	23.8 [22.4]	" [423]		
24	3.0	0.38	23.8 [22.4]	321 [482]		

^aThe measured stream flow data reflect the base of flow during the second discharge experiment at point 17.30 km, which corresponds to 1.5 km below the Mf location. The adjusted stream flow values take stream dilation by the location of ground water into consideration in estimating gas transfer velocities. Using the unadjusted and gas sampling Mf data with measured stream flow data, the gas exchange transfer velocities calculated for the second experiment between the island and offshore spring areas are 0.1 m/d and 19.0 m/d, respectively. Since the adjusted discharge values are used in the calculation, however, negative gas transfer velocities of -12.1 m/d and -1.0 m/d are estimated for the unadjusted and gas sampling Mf data, respectively, not available due to questionable data.

higher the temperature, the faster the gas exchange process. To enable to compare gas exchange coefficients for different gases or to use one gas exchange coefficient to predict another a dimensionless ratio, the Schmidt number (Sc), was used (Bedell, 1964; Neeselink, 1965; Enoch, 1994). The Schmidt number is defined as the kinematic viscosity of water (ν) divided by the molecular diffusivity of the gas (D). Since both ν and D are temperature dependent, the Schmidt number corrects for the temperature and species dependence of the gas under consideration (Vander et al., 1997; Neeselink, 1998). The Schmidt numbers for CO_2 , NO and O_2 for temperatures ranging between 10 and 27 degrees Celsius are found in table 12.

There are many models available to describe the relationship between the gas transfer velocity (K) and the Schmidt number (Sc) (Malpassick et al., 1998). In this work, the correction of the exchange coefficient is based upon equation 9:

(9)

$$K = K_{Sc=1} \cdot Sc^m$$

where:

$K_{Sc=1}$ = transfer velocity,

Sc = Schmidt number;

$m = -0.5$ and depends on the turbulence at the air/water interface;

Table 13. Comparison of diffusion numbers for CH_4 , CO_2 , and N_2 at selected temperatures.

Temperature °C	DF_2	DF_{CO_2}	DF_{CH_4}
10	128.8	104.0	9.49
20	82.0	82.0	9.31
30	74.2	67.0	4.19
40	69.0	49.7	3.76

The saturation coefficient was calculated using the following equation (from Nittrouer et al., 1983):

(104)

$$S_0 = k \cdot (DF_2 / k \cdot (DF_2/DF_{CO_2})^{1/2})$$

where

S_0 = saturation coefficient, day⁻¹;

k = gas transfer velocity, m/day;

h = average stream depth, m;

DF = diffusion number for the indicated gas at 20°C (either temperature of the river).

The Santa Fe River's gas transfer velocity and corresponding saturation coefficient is 0.03 day⁻¹ and 0.7 day⁻¹, with $w = 0.10$ m, $h = 0.1$ m, $q = 45.0$ day⁻¹, and $k = 10^{-6}$ in the eastern reaches of the river. Table 13 provides a comparison of saturation coefficients from Thibault and other sources using variable factors. Only a variety of factors the saturation coefficients based on DF_2 measurements are within the same order of magnitude as S_0 .

values given for other streams with the exception of the most part of the Miller Branch, oak ridge TW. The typical K_1 values range from 110 to 130 day⁻¹, using MF_{10} , propane and others as gaseous tracers (Bennich et al., 1991; Bencivenga et al., 1992). Therefore the K_1 values for this stream are about an order of magnitude greater than other published values for different streams.

Many predictive equations have been developed for specific streams that permit estimation of gas transfer and gaseous coefficients. These equations typically relate gaseous coefficients to several easily measurable physical and hydrologic parameters of a stream. Table 14 shows gaseous coefficients (K_1) values determined for the two river reaches based on different predictive models available in the literature. The calculated K_1 values vary considerably. None of the equations reference in Table 14 were suitable indicators of the gaseous coefficient determined for the first Santa Fe River experiment, through extrapolation. The basic statistics for the predicted K_1 values for this reach were a mean of 2.00 day⁻¹, a standard deviation of 2.00 day⁻¹, and a median of 0.15 day⁻¹. If these statistics are compared to the value estimated from the MF_{10} tracer experiment (16.7 day⁻¹), it can be concluded that all these models underestimate K_1 for this reach of the Santa Fe River.

Table 13. Comparison of selected stream restoration quantifications determined through the use of volatile tracer (from Ritter et al., 1993).

Stream	T (m/s)	D (m)	G (m ³ /s)	N ₀ (s ⁻¹)	N ₁ (s ⁻¹)	Concen %	t hr	Ref.
Watauga	0.09	0.4	0.79	14.0	0.12	expt.	10	1
Watauga	0.40	4.1	26.0	0.3	1.02	expt.	10	1
Roanoke	0.09	0.3	0.05	7.4	0.10	proposed	25	3
Watauga	0.30	0.30	0.03	12.0	0.10	expt./prop.	27	3
Roanoke								
River St.	0.09	0.09		0.3	0.10	expt.	10	4
W. Forks/ Watauga R.	0.09	0.30	0.06	12.0	0.10	expt.	25	4
W. Forks/ Watauga R.	0.1			12.0		proposed		7
W. Forks/ Watauga R.	0.3			12.0		proposed		7
Roanoke	0.09	0.31	0.06	2.4	0.1	proposed	9	4
Alligator Creek, FL	0.30	0.31	0.1			proposed		8
John River R., FL	0.09	0.09	0.1			proposed		8
Cowberry CR., Oconee, FL	0.09	0.07	0.05			proposed		8
Perdido R., FL	0.09	0.09	0.05			proposed		8

References

1. Ritter, 1984
2. Grant and Ritterhouse, 1980
3. Ritter and Fung, 1979
4. Palivoglu, 1997
5. Ritterhouse et al., 1993
6. Duthie and Ritter, 1994
7. Gartman et al., 1993
8. Thompson and Ritter, 1993

Table 14. Comparison of stream retention coefficients K_2 (day $^{-1}$) determined through the use of ST, with values derived from predictive models (from Ellingsen et al., 1993).

Reference	Series (a) River	
	River River	Run Index
O'Connor and Robbins, 1970	2.2	2.9
Brownell and Ulrich, 1988	4.3	4.3
Chardillier and Helfferich, 1970	4.7	3.3
Davis and Sandy, 1988	1.8	3.1
Hooper and Reynolds, 1989	2.7	2.8
Jackson and Shugart, 1971	1.2	1.6
Russel, 1973	0.8	1.0
Bennett and Robbins, 1973	2.4	3.0
Bennett and Robbins, 1973	2.0	4.3
Postma and Penney, 1973	1.8	3.0
Chardillier et al., 1982 (1)	4.2	2.8
Chardillier et al., 1982 (2)	1.8	3.4
Leopold and Parmenter, 1945	1.8	3.1
Quinn et al., 1984 (1)	2.4	3.8
Quinn et al., 1984 (2)	2.3	3.9

CHAPTER 3 METHOD AND CONCLUSIONS

Method

In the hyporheic zones of the western Santa Fe River basin, measuring mixing parameters of the stream is made difficult by the numerous springs, seeps, upwells and boils found within the Santa Fe River. These detailed mixing experiments were devised to address the variability in the volatile dissolved gases, natural carbon-13 (^{13}C) and artificial sulfur hexafluoride (SF_6).

These experiments revealed that 1) sulfur hexafluoride is an efficient and useful stream tracing agent than allows for the characterization of stream parameters such as velocity, mixing (lateral, vertical, and longitudinal), and spring influence; 2) the injection of SF_6 into a region with no prior knowledge of springs or upwells may also indicate the location of such features; 3) naturally occurring ^{13}C can also be used to interpret spring incidence and mixing characteristics throughout a stream cross section; 4) concentrations of ^{13}C increased with depth and appear to be dependent upon source area; 5) the overall average stream section concentrations correlate well to both the vertical and longitudinal samples taken at the midpoint of the stream.

and (3) future river water sampling should be done in an integrated fashion to account for concentration variations that may occur in the stream water section, even though complete mixing is assumed in the reach of the river.

Tracing

A previously reported ground water, gamma tracer, ^{137}Cs , was introduced into three sites, three sites and three-meter rate on three different occasions in order to establish travel rates through the park and detect possible points of input from ground water. The tracing experiments demonstrated that (1) the tracer could be moved through a single outlet in the top surface of the park; (2) the river flows at a constant rate through the park and intersects each consecutively and continuously downstream of three sites to the River Ries; (3) mathematical equations used normally to predict the rate at which surface water moves within a stream are applicable to estimate the rate at which ground water has moved through the park, supporting the idea of no-ground flow conditions.

Flow component

The multiple application of various tracer rates revealed the location of a significant source of ground water to the system beyond site three. In addition, it was

(most likely 1) the temperature data provided as much useful information as the other more complicated techniques and 2) was also useful in a conservative nature to estimate the selective mixing of surface and ground water; 3) temperature, geochemical, rates and oxygen isotope data show documenting the distribution of and connections among ground water, surface water and artesian water; 4) because of the rapid nature that the Santa Fe River and ground water moves through O'Leary State Park (about 1 day/ney) and the depth at which the water appears to be moving, about (20 m below land surface) the artesian located throughout O'Leary State Park do not largely contribute to the underground system of the Santa Fe River.

Discussion

Utilizing the decrease in $\delta^{18}\text{O}$ concentrations along the two reaches, a gas transfer velocity of 21.8 m/d and a K_t value of 15.7 day⁻¹ were calculated. These values are within the same order of magnitude as other streams reported.

It was determined that 1) ^{35}Ar is unacceptable as a tracer because it has a much lower diffusion coefficient and incomplete mixing of ^{35}Ar enriched ground water delivered by numerous springs and seeps creating complex cross-stream and vertical concentration gradients in the river; 2) stream channel characteristics caused the rate of gas transfer, along short intervals of a few hundred meters between

sampling locations in the river, to have a high degree of variability; 3) gas exchange experiments should be completed in river length long enough to average in channel morphology as well as hydrologic characteristics; 4) river mixing prediction equations to estimate gas transfer and reaeration constants are site specific, it is difficult to apply these in different hydrologic settings.

Conclusions

An attempt to develop a computer model of the study area was complicated. It was determined that due to the complex hydrogeologic nature of the basin and the inability of current computer models to address specific hydrologic parameters, computer models are not suited to adequately characterize ground water and surface water conditions.

References

The results of this research confirmed several aspects of SF_6 . Most importantly they indicate that 1) SF_6 is chemically and biochemically inert, capable of being detected in extremely low concentrations, and is well suited for water testing and mixing applications in karst terrain; 2) In comparison to fluorescent dye tracers, such as rhodamine B , SF_6 has the advantages of detectability at low concentrations and none of the interference problems associated with organic dyes, dissolved particulates, and

equilibrium material that can occur with fluorine over 21 $\delta^{18}\text{O}$, has the potential as a quantitative tracer under specific closed conditions. 4) δF , may also be applied to geochemical problems such as well compatibility studies, and detecting against corrosion through a containing layer. The down sides of δF , are that 1) construction of the analytical equipment is a mess; 2) it is a volatile tracer and is lost quickly to the atmosphere and 3) sampling δF , is often time consuming and labor intensive.

Human development in the Illinois State Park

The landscape within the western parts of River Park is a snapshot in time. The time scale of the park's evolution is many orders of magnitude slower than that of man's human civilization. Some limestone in the park are relatively young, such as the Miss. others are vastly older, carved perhaps by the slow sculpturing of limestone since the early Tertiary. Determining the time at which events occurred to develop the park is difficult.

Historical factors such as temperature, sea level, ocean dioxide levels, rainfall, and depositional environment have varied drastically since the deposition of the Illinois Limestone that underlies the park and houses the conduit system for the parts of River Park and surface limestone cover over of the bluffs; the difficulty is unravelling the record (White, 1990). The conduit system within the park

not yet been explored and described in detail), and thus leaves many questions unanswered about the nature.

Based on these experiments and surface textures it has been determined that Ojene sink is the initial sinking point of the Banks Pa River. The river trends at about 1.5 km/day, underground, in a single cavity and periodically returns to surface and then disappears at several points along the upper reach. Up to Ojene sink there appears to be little ground water connection to this flow. Downstream of Ojene sink there is more ground water mixing with the Banks Pa River and the flow becomes more diffuse. The river variability increases at the River Blue with a greater land and temperature signal much more like that at ground water rather than surface water.

The age of the surface sinks may be estimated by the age of the surrounding sediments that surround the sinks. For example, where the sink opened there are no well developed eggtraps, an obligate wetland species, taking over 10 years to complete, surrounding Ojene sink. There are many eggtraps here with a high fort diameter trunks making this sink a much older feature. Also, if the trunks of the eggtrap trees appear to be drilling into the sink this may indicate that either the sink is migrating in the tree direction or that the sink opened after the establishment of the eggtrap trees. Using these two lines it may be possible to estimate an age relationship among the various sinks in the park and

thus a relationship between the marsh system and the wetlands found within the park. That is, the older wetlands would indicate the older marsh tendencies and describe how in what directions, and at what rate the park developed.

The general abundance of sedge and marsh domes in the upper marsh of the park versus the downstream end of the park indicates that the upper marsh is more active. The reason for this higher activity in this part of the park may be due to two things. First, the upper marsh has only one outlet for the water it holds. If there is only one outlet for the same volume of water that flows through the lower marsh of the park, it must be larger, and is therefore more likely to interrupt the surface creating a depression and new tendencies. Second, the nature of the water in the upper marsh is that of surface water. This water is more unstructured with respect to σ^2 , and is more capable to erode the underlying limestone.

New sink has migrated to the north about 50' over the past two years. This process will continue as the small sink converges with larger sinks and new sinks continue to appear along the pathway of the underground route to River. The upper marsh of the park will more quickly become a surface feature for the water in river and perhaps this sink will eventually appear to be the starting point of the Santa Fe River in the future. Accompanying the development of the larger surface feature, wetlands will also coalesce

lining the banks of the new portion of the river and appear much like that of the eastern part of the north the river: *Barbilla.*

APPENDIX B
THE CHRONOTAGHET AND THE TELEVISION POST STATION

Gas Chromatography and the Infrared Part 2

Introduction

This section provides the basic instructions to operate the Shimadzu gas chromatograph (GC) equipped with an electron capture detector (ECD) for the analysis of sulfur compounds. It gives a brief overview of the component parts of the system but does not go into detail about their construction, design and specific functions. This section will provide the user with a basic working knowledge of the equipment but the user should at no time attempt to "fix", or "repair" the instruments without further consultation or assistance from someone who is more capable of doing so. The equipment is expensive and extremely sensitive, therefore even the slightest wrong adjustment or manipulation of the system can render the system out of commission for months and require expensive repair. It is also important to read all of the instructions before attempting to run the system.

It is also should there be any type of petroleum product in the lab, even if the GC is not being used. This especially applies true for ~~water~~ and other organic products. Smoking is also strictly prohibited from the lab at any time.

Also, because of the sensitivity of this system the setup of the system may take one or more days to accomplish.

Therefore, if planning an experiment, make sure to start the system running at least 14 hours before analysis is to occur.

Operation of the GC system

The GC system has been designed so that repetitive SF_6 analyses can be completed efficiently and relatively quickly. If the system is operated properly, approximately 10-15 samples can be analysed in one 8 hour period. The analyses can detect SF_6 in concentrations as low as single parts per trillion with a precision of 1%.

Equipment

There are six component parts of the entire gas chromatographic system. All parts must be in correct working order or the analyses will not be able to be completed accurately, if at all. With reference to figure 12, the system consists of: 1) a (two) litre high pure grade nitrogen tank, 2) electronic-flow gas purifier, 3) multi-port injection syringe, 4) gas chromatograph, 5) Integrator, and 6) a SF_6 standard tank.

Equipment functions

1) Nitrogen tanks.

A) These tanks serve as the source of the carrier gas for the sample or gas injected into the GC. This gas will

essentially push the sample gas through the system to be first separated and then analyzed.

b) This tank acts as the source of gas which is used to fill the burettes of the syringes which holds the other samples. Once shapes the SF₆ will diffuse into the burettes of the syringes and then be injected into the syringes.

c) Clean-up/last gas purifier.

This component removes any contaminants that may be in the carrier gas.

d) Multi-port injection system.

This component first separates individual gas components in the sample gas and then consistently delivers equal amounts of injected sample gas to the detector analysis.

e) Gas chromatograph.

This component measures the amounts of individual gases found in the injected sample gas.

f) Interpreter.

This component interprets the data gained from the GC and provides a printout of the relative amounts of gases found in the injected sample gas.

g) SF₆ Standards.

The standards are known concentrations of SF₆. They are used to generate a calibration curve by which sample

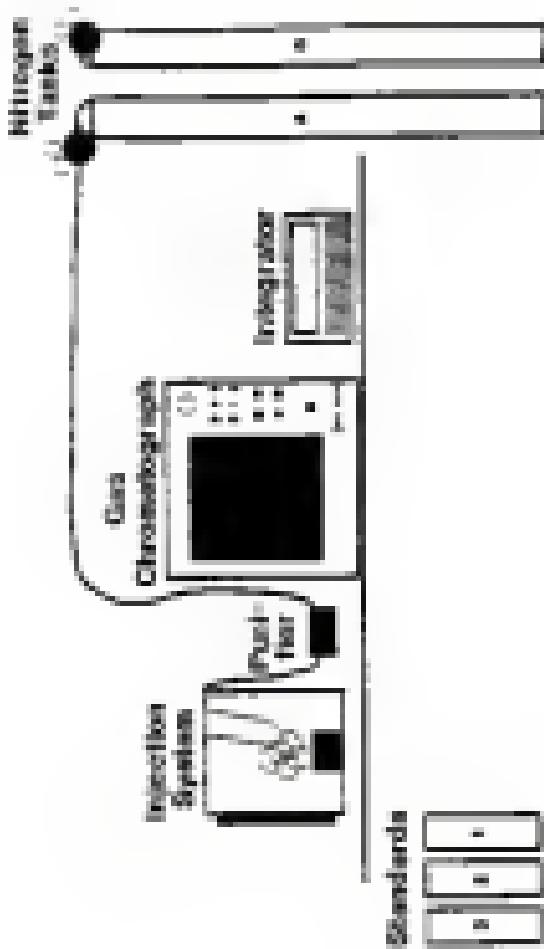


Figure 10. Gas chromatograph used for MP₃ analysis.

data will be compared to, to obtain actual concentrations of NO_2 .

General Procedure

Before beginning to turn anything on there are several items that should be checked. Also take a minute to familiarize yourself with the individual components of the system. The items that need to be checked include:

- 1) that there is enough paper in the integrator,
- 2) that there is ink in the ink jet printer on the integrator,
- 3) that there is nitrogen, at least 100 psi in each tank,
- 4) the glass purifier. It should be black with none broken at each end. If it is totally broken it needs to be replaced,
- 5) that all equipment is plugged in properly,
- 6) that there is a straight tube hanging from the injection port. If it is not there one will have to be made. It consists of straight, glass wool and tygon tubing (Figure 14),
- 7) make sure that there is water in the beaker and add to the wash-port system and push the tygon tubing to the bottom of the glass.

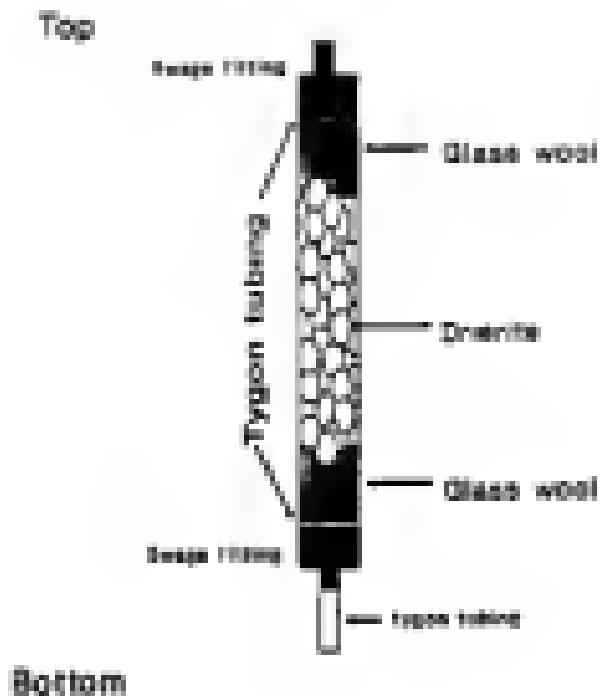


Figure 10. Cross section of dialyzer tube used in SR_a analysis.

Regulation procedure

1) Turn on the N_2 tank (far left in Figure 4b) then turn on the ac system and adjust a flow rate to about 20 psi on the left dial of the regulator. To turn the tank on, simply turn the top tank handle counter-clockwise until it is all the way open then turn it back over half of a turn, watch the needles on the two dials to see if they respond. If not, the pressure going out of the tank turn the tank handle on the regulator clockwise to increase the amount of gas. Leaving the tank, the 100% pressure gauge should be set between 30-33 psi.

2) Turn on electronic-flow gas purifier.

3) Check, using "scope", around any steel or copper connections for leaks in the system.

4) Open all capped screws on the multi-port injection system.

5) Purge the system for one hour.

4) Multi-port Injection System: Figure 4b, adjust flow rates using knobs marked A and B on the multi-port system so that the flow rates on the left of the multi-port system is equal to the 5 ml bubble meter on the right side of the multi-port system. Once they have been adjusted to the same

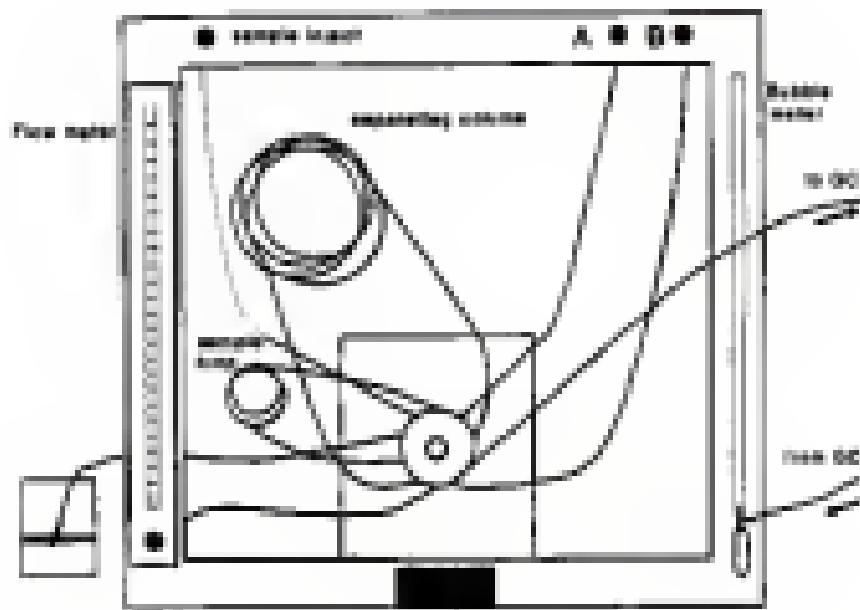


Figure 40. Multi-port injection system for H₂ analysis.

flow rate adjust the needles on the nitrogen tank so that they read 00/00. It is important to move the switch from load to inject on the multi-port system and switch in such location that the flow rates are the same. Note, this may take some time, be patient! The flow rate on the flow meter is determined by comparing the number to which the floating ball rises up to, to the pink sheet of paper posted on the wall behind the system. The number on the flow meter is not the flow rate, the flow rate is the number written on the pink sheet under the "flow" column. The flow rate on the bubble meter is determined by comparing the lower tube rises with epoxy and timing how long it takes to rise to the 5 ml mark on the tygon tubing. Then, by using the flow rate table determine the flow rate through the tube.

7) DC adjustments (the entire system is located in the DC box located to the left of the system): turn on the DC and set the upper temperature dial, (inject temp) to 320 by rotating the small dial to the left of the setting and set the lower dial (oven temp) to 10, using the oven procedure. Always make sure that there is nitrogen going through the DC when it is running.

- 8) Leave entire system running for about 2 hours.
- 9) Readjust flow rates on both meters and adjust if needed.
- 10) On the front of the DC, the lower most dial (marked attenuation) should be set on 1, the current level

should be set on 1.0, the bias button should be set on 1 (operated by) ..

12) Integrator adjustments (a copy of the first page of the manual is found in the appendix, the entire manual is located in the SC box located to the left of the system): turn on integrator, the switch is located on the back right of the machine near the plug into the machine. First the machine will go through its own startup check and give a relatively blank screen. Once in stage 0 it will say wait for you connected. Hit the LCD START button, this will bring up a new display on the screen. This is the screen that you almost always want to have displayed. At the top of the screen several letters will be displayed including the

CH 01 RDM RDM 08 00000000000000000000000000000000

the meaning of each symbol is:

CH = channel, should be set on 8.

RDM = data name,

RDM = whether the printer will print automatically (AUT0), on (ON) or off (OFF)

CH = chart speed, (in cm of paper printed per minute) 10 should be set on 3.

ATTEN = attenuation, this is basically a filter adjustment of the signal transmitted into the integrator from the SC, set at 20.

TIME = keeps a running time of how long the Integrator has been working.

LEVEL = the relative strength of the signal being transmitted to the Integrator.

13) Depress the ADJUST button on the Integrator and then type "12" and hit the ENTER button and then hit the LCD DISPLAY button.

14) Now carefully, if anything is going slight, all major adjustments have been made.

15) Read the Level on the Integrator, it should be reading quite high at first and may take several minutes to have to days to adjust to a level of good which is what you want. If it is not at 1000 or even close try adjusting the coarse adjustment knob on the CC, to get the level down to 1000. If that succeeds then switch the Load/Inject button on the multi-port system to the opposite position, you will notice that the level will drop probably significantly and may stay there for again minutes, hours or days? If you are lucky and the level responds quickly back to around 1000, try using the fine adjustment knob to get it to be exactly 1000 and have it remain there. If this happens, then again switch the Load/Inject button to the opposite position and read the levels. It should eventually come down to 1000. AGAIN this procedure has been known to take days to reach equilibrium so do not expect any glorification and be patient.

16) If the levels do not come down within a day or so

do not stretch the system from a problem and should not be used any further.

14) If the levels have equilibrated to 2000 on both the inject and load valves and the flow rates remain constant in both inject and load valves the system is now ready for use. One final step before continuing is to hit the μ button on the Integrator. If you hit the μ EVAL button, this will evaluate the amount of "sales" going through the GC, the integrator is now thinking and is averaging out the amount of sales going to the Integrator, this process takes a couple of minutes. You will know when it is finished when it prints out something like $\mu = 100$. The μ value should be less than 100, if not then the system is not ready to be used. This procedure should be repeated for both the load and inject valves on the multi-port system.

Now assuming all is well, i.e. levels at 2000, flow rates good, $\mu = 100$, you can proceed with an injection. Injection of a gas sample occurs via a glass syringe, this is true for all samples but glass syringes are not used for analysis of standards.

17) Inject the standards. First make sure the inject/load switch on the multi-port system is set on load.

18) To complete a series of standards begin with standard one. This should be marked on the tag on the tank.

19) Turn on the standard tank, by turning the knob on the top of the tank. Next open the three-way-stop-cock on

the end of the standard tank hose. Now insert the end of the syringe hose into the types tube of the syringe which should be fastened to the multi-port injection system at the position indicated "sample inject".

20) Now slowly move the tip of the hose and watch the glass filled with water to see if system standard is exiting the system. This should be a slow and gradual process and not last more than a second or two. In other words do not inject gas through the system let it escape slowly. What you are doing is filling up the sample loop with a specific amount of gas and excess gas is added to the water.

21) Wait 10 seconds, then simultaneously switch the load/Inject button to inject and hit the Interpret A button on the Integrator. If done correctly the printer should be spooling and begin plotting a relatively straight line.

22) At about 0.60 to 1.1 minutes into the injection the printer should be printing a large peak on the graph. Once the peak has been completed and returns to base level hit the Interpret A button again and switch the load/Inject switch back to base. At this point the Integrator will begin to print out the integration results from the sample and will also temporarily store it in its memory. At this point write on the printed paper the sample number where the print out occurs.

23) If all has gone well, the levels should readjust back down to around 1000. If they do not do so immediately

Let the machine run in the stand mode until it does about (about 3 injections), or it does not come back as fine than obviously there is a problem in the system, most likely it is some type of contamination, and no further use of the machine is recommended.

34) Repeat steps 31-33 until the area printed out on the paper is approximately to 30, then move on to standard 1 and then 2 following the same procedure.

35) Injections of samples with syringes (Figure 46). The syringes should be filled with a water sample in excess of 10ml. Only the samples that are filled to greater than 10ml and have no air bubbles in them should be used, but do not throw out samples with air bubbles or ones having less than 10ml or water because they may be able to provide some qualitative data for the experiment.

36) The first step in the process is to remove the excess water in the syringes by slowly opening the three-way stop cock and pushing the water out the end up to the 10ml mark on the syringe. Next, open nitrogen tank "A" and allow some excess nitrogen flow out so that you can just barely hear it escaping. Now fill the top 10ml of the syringe with nitrogen. Carefully, insert the tip of the syringe into the tygon tubing attached to the nitrogen tank, and very slowly open the three-way stop cock to allow nitrogen to push the sample and syringe piston down ward. Be careful not to open the stop cock too quickly, you may break the sample and

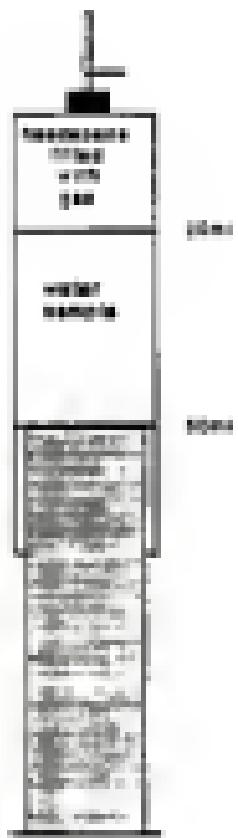


Figure 44. Glass syringe used for injecting SF₆ gas.

plate on the floor. Now allow the nitrogen to fill up the top (lit) in the springs, so that the top of the plate should be at the 50% mark on the springs. Shut the stop cock and then turn off the nitrogen tank.

17) Now shake the springs carefully but vigorously for 2 and 1/2 minutes. This procedure causes the CO_2 to enter and mix in the headspace of springs.

18) Next, make sure the multi-port switch is set on load, insert the tip of the syringe into the drying column, open the stop cock to allow only the gas in the headspace to enter the drying column. At this time you should have some support of the bottom of the plate so that it does not drop. Now slowly and steadily push the gas and only the gas is through the system. There should be some excess gas exiting into the glass beaker to the left. Once you have pushed the gas through the system close the stop cock and take it out of the drying column. Wait 10 seconds and then as before, simultaneously left the INJECT A button on the integrator and switch from load to inject on the multi-port injection system.

19) Follow the same procedures in steps 13 and 15.

20) Repeat with more sample springs following steps 16-18. Consistency on filling the headspace exactly to the same level with each springs, injecting at the same rate, shaking the springs for the same length of time are all crucial to obtaining accurate results.

11) After 8 to 10 samples have been run, run one standard run, and make sure it matches with the standards run earlier. If it does not match you (a again or run another standard. If still nothing is repeated correctly, do not proceed any further.

12) Shut down of system. Once all of the samples have been run and standards have been run at the end of all the samples, now its time to shut the system. The system should only be shut down if no samples are going to be run over the next week plus. If more samples are intended to be run the next day or even within a week or so it is best to leave the system running with all equipment left on.

13) However if no samples are to be run, follow these steps strictly. First, turn off the GC and the Integrator. Allow the GC to cool for at least three hours or preferable over night. Second, remove the drying column from the sample inject port, and cap the port with a sweep cap. Third, turn off the nitrogen tank 45° and the nitrogen tank purifier, and allow the nitrogen tank bleed off all excess gas. Fourth, remove the lines exiting from the bottom left side of the GC and cap the GC port with a sweep cap. Fifth, put all tools, papers, and sample sheets away, and when all needles and syringes are place them back in their appropriate places.

Trouble-Shooting Tips...

There are many things that can go wrong with this system, but fortunately if the system is set up properly and great care is taken for the system, especially when reconnection is concerned it does not break down often. However when something does go wrong, nothing can go by trying to solve the problem.

Any "normal" problem can be fixed often with little effort. A comprehensive guide to trouble shooting is provided in the GC reference notes located to the left of the system. It is entitled "TROUBLESHOOTING GUIDE: HOW TO LOCATE THE CHROMATOGRAPH PROBLEMS AND SOLVE THEM YOURSELF", issue 7700, by Supelco. By looking through this guide many small problems can be located and taken care of. A copy of the front page is found in the appendix.

Take-Off Procedure

The take-off procedure is the technique used on the GC and separating column to recondition the column to enhance the performance. The procedure takes place in the GC oven. It is completed by following these steps:

- 1) If the GC has been running now in off, and open the GC oven door, but continue to let the nitrogen gas flow through the system. Let the GC cool for about two hours or more.

- 2) Once it has cooled, disconnect the column from the

multi-port injection system, and cap the openings left on the multi-port system.

3) Disconnect the main nitrogen gas line from the injection board and route it so that gas is flowing directly into the GC and bypassing the injection board completely.

4) Turn the oven off and disconnect the fitting upstream of the empty vial being used and insert the vial in this spot in the line. Reconnect the vial to this spot and tighten all fittings. Check for leaks using soapy and correct them if needed.

5) Close the oven door and lower the flow rate of nitrogen to 10 psi, by adjusting the top handle on the nitrogen tank.

6) Set the Inject temp to 300.

7) set the oven/valve temp to 10 and let run for one hour.

8) next set the oven/valve temp to 110 and run for one hour.

9) Finally set the oven/valve temp to 210 and run for one hour.

10) now turn off the GC and open the oven door. Let the system cool this at least two hours.

11) remove the vial and replace it on the injection system, reconnect the steel tubing in the oven, and

reconnect the copper tubing to the original location on the injection system.

(b) After all connections have been made, check everything on the system with soap and begin the startup procedure for running the GC system.

APPENDIX B
ME₂ ISOPROPYL BISPHENOL

SR-1 Injection System

Previous attempts were made by R. Blasch and T. Rinehart to artificially design an injection system that would deliver at a consistent rate the dry-stocked river water to the river. The design had to be field sturdy, easy to transport, relatively inexpensive, and most importantly dependable. The final design was reached after numerous attempts and was only slightly modified after nearly two years of continuous use. The design includes: A) a 7000-lb. SR, tank, B) a two stage regulator, C) 300 liter plastic barrel, D) a portable pump, E) a 12 volt battery, F) 1100 ft. 0.625 in. tube tubing, and several 3 pound lead weights (Figure 47). The general theory was to saturate water with SF₆ and then inject the water into the river or lake. Previous experiments that injected the SF₆ directly into a water had problems of gas loss immediately to the atmosphere (personal communication, R. Rinehart, 1981).

In most cases the injection system would be set up and tested in the field the evening before the experiment was to take place. The general set up procedure involved first filling the 300 barrel with river water by hand pumping

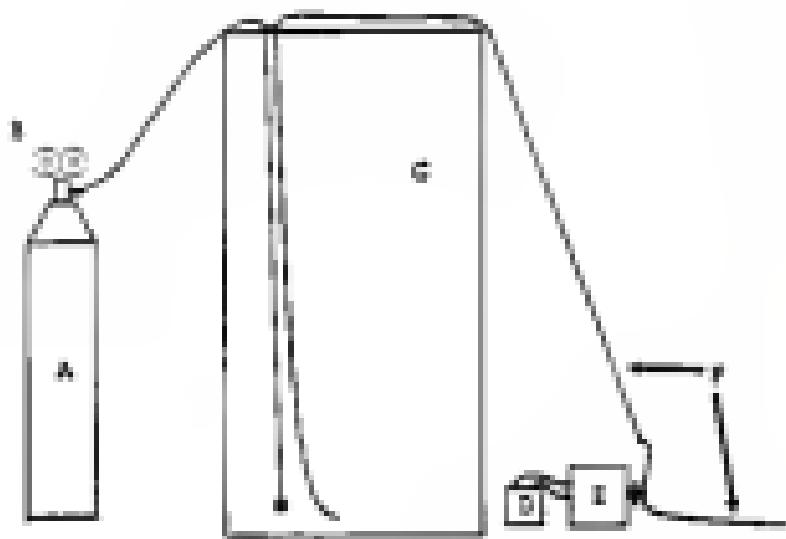


Figure 47. SF₆ field injection system used throughout all injection experiments.

five gallon buckets of river water into the top opening of the barrel. The next step would be to connect a one meter piece of tygon tubing to the copper tubing that already was fitted with a diffusion stone at its end. The end containing the diffusion stone was first threaded through a rubber stopper and then into the barrel, where it lay nearly at the bottom. The opposite end of this piece of tygon was connected to the two stage regulator that is controlling the addition of SF_6 to the barrel.

Next, another two meter piece of tygon tubing was threaded through the same rubber stopper and placed at the bottom of the barrel. The opposite end of this tygon tubing was attached to a "T" fitting which controls the flow going into the peristaltic pump. On the out the side of the peristaltic pump, two separate, appropriate length pieces of tygon tubing were then snipped out into the water, and held at the bottom with lead weights. The peristaltic pump was then connected to the 12 volt battery and the system is complete for injections.

The initial phase of injection involved saturating the river water in the barrel with the SF_6 . The SF_6 would vigorously be injected into the airtight barrel for about ten minutes. After this, the two stage regulator would be turned down so that the total pressure on the regulator read about 2-3 psi. By continually allowing SF_6 to enter the barrel, it assured complete saturation of the river water.

Throughout the injection, after twice the glaciolite barrel was saturated with the increasing pressure up to the 4F, had to be turned down.

Once the water was saturated, after approximately five minutes, the percolation pump was turned on and the water would then begin to flow from the barrel to the river. During most occasions particulate matter that had been transferred into the barrel would be seen moving through the glass tubes taking guarantee that the water was actually being injected. The injection rate for the aqueous media was approximately two liters per minute, which allowed for an initial 4 hr. flow injection.

APPENDIX C
CANNON BOTTLE INFORMATION

the cleaning process consisted of first rinsing the bottles in deionized water, second the bottles were then filled with three normal nitric acid and left standing overnight. Next the nitric acid was emptied and then the bottles were rinsed thoroughly with triple distilled water. These bottles were left to air dry, capped and then ready for sampling. Water samples were again taken at about 0.01 m where possible. The dirty milliliter collected sample was then packaged for transport back to the lab for analysis.

REFERENCES

Blay, T., 1982. Techniques for Analysis of Fluorapatite and Hydroxylapatite by X-ray in Water or Dissolved Suspensions. *Underground Laboratory Circular*, Little Rock, AR.

Billetter, R. and C. Müller., eds., 1973. *Fluorapatite Weathering Aspects, Environmental Stability and Safety*. Supplement 7: 19, New York, American Society, 216 p.

Brinkmann, R., 1981. state of disequilibrium between ^{187}Re , ^{188}Re and ^{188}Os in groundwater from bedrock. *Geochim. Cosmochim. Acta*, 45:600-604.

Brink, W., van der Velde, R.H., and van Ginkel, J.M., 1984. Role of groundwater in shaping the Eastern Coastline of the Mexican Peninsula, Mexico. In: *Groundwater as a Geochemical Agent*, R.G. Lefèvre (ed.), Berlin, Akademie-Verlag, p. 289-312.

Brown, R.H., 1977. Atmospheric reservoirs in natural systems. *Water Research*, 11(1):749-760.

Bruck, R.P., 1984. A generalized genetic framework for the development of aquifer and karst in Florida, USA. *Environmental Geology Water Science*, 5(1/2):13-18.

Brownell, J.P., and R.L. Mathews, 1973. Reservoirs in open-channel flows. U.S. Geological Survey Professional Paper 727, 75 p.

Biddlecom, A.H., 1982. hydrogeology and karst development of the Tuckerman River Area, Alachua County, Florida. M.S. Thesis, University of Florida, Gainesville, 113 p.

Bruck, R.P. and R. Scott, 1984. chemical character of Florida's waters -- 1981. Florida State Board conservation division, water survey and research report 8.

Bruck, R., 1979. An investigation of the ^{187}Re - ^{188}Re disequilibrium in the natural waters of the Santa Fe River area of north central Florida. Ph.D. Dissertation, Florida State University, Tallahassee, FL.

Brooker, W.H., 1991. An application of natural ratios to problems in water circulation. *Proceedings of Conference in Ground and Fresh Waters, New York, International Hydrogeology Observatory, Palisades*, p. 128-136.

Brooker, W.H., Y.H. Li, J. Cromwell, 1997. ^{36}Ar and ^{38}Ar Concentrations in Atlantic and Pacific Oceans. *Hydrogeology*, 1997(12):1207-1213.

Brooker, W.H., 1991. Hydrogeographic divisions of Florida and accompanying guide. *Institute of Land and Agriculture Sciences, University of Florida, Gainesville, Florida*.

Berry, A.W., Bobrovsky, B.M., and G.J. Bensler, 1977. Current status of Soviet safety and environmental aspects of fluorine-containing substances used in detergents in the United States. *Critical review in environmental control*, 7(1):1-19.

DeGelleckler, T.J. and R.J. McConnell, 1999. A multivariate analysis of reservoir data. *Water Research*, 33(10):1943-1951.

Dorpal, R., Hoopp, R.H. and T. Pausen, 1991. The quality and water resources of the Upper Tennessee River basin, Florida. *Florida Geological Survey, Report of Investigation 87*.

Donaldson, R.A., Elmore, R.L., and R.A. Buckles, 1944. The production of reservoir data. *Journal of Hydraulics Engineering Division American Society of Civil Engineers*, 70(10):111-118.

Clark, W.F., Hespere, R.H., Morris, G.C., and J.S. Siegel, 1994. Water Resources of Alachua, Bradford, Clay, and Union Counties, Florida. *Florida Geological Survey, Report of Investigation 10*, 378 p.

Cromwell, J.H., Coffin, T., Dohrt, F.H., and Lutze, R.H., 1974. Classification of natural and reservoir radon data of the United States. FES/ERD-74/1, U.S. Fish and Wildlife Service, Office of Biological Services, Washington, DC, 128 p.

Cromwell, J.A., 1998. Memorandum of April 16, 1998, from the Director of the Criteria and Standards Division, U.S. Environmental Protection Agency, to R.H. Cromwell, Director of the Water Management Division, Region IV of the EPA concerning radon W7 and S (from available, with 2-page discussion, as FEDERAL REGS., Bulletin 102, from Turner Design, Inc., 247 Old Postoffice Rd., Mountain View, CA 94031).

Boggs, G.B., Boggs, G.B., Reid, R.O.L., Galante, M.P., Madala, J.A., and E.B. Riesert, 1993. Comparative measures *in vitro* and *in vivo* studies on the mutagenicity/mutability of radon in water. *Mutation Research*, 298:227-239.

Boggs, G.B., Boggs, G., and J. Robert, 1995. Subacute arsenic and barium pollution in the West Florida continental shelf: disparate environments and similar outcomes. *Geological Society of America Abstracts with Programs*, 17:545.

Brown, R.P., and R.P. Bassett, 1984. Distilled/boiled/boiled distilled (DBB) as a treated for nitrate-nitrite removal from a nitrogen enriched river. *Env. Monit. and Assess.*, 4:111-120. *See treatability of river waters*. Kingman, Mass., R. Reid, p. 293-303.

Ellins, R., 1990. The application of ^{226}Ra in measuring groundwater discharge to the Meramec River, Missouri. *In: Proceedings of the International Symposium on Tropical Hydrology sponsored by the American Water Resources Association*, Miami, FL, May 1990.

Ellins, R., 1992. Utilizing groundwater radon to a portion of the Big Branch de Meramec River basin in Missouri. *Env. through the measurement of ^{226}Ra* . *In: Proceedings of the Third Southwest Islands Water Resources Congress*, U.S. Virgin Islands, Miami, FL, July 1992.

Ellins, R.R., 1993. Terrope hydrology of karst drainage basins in Missouri and Puerto Rico. Ph.D. Dissertation, Columbia University.

Ellins, R.R., 1995. Tracing ground water and surface water in the eastern Santa Fe River basin using ^{226}Ra and ^{228}Ra . *Proposal to the National Science Foundation*, University of Florida, Gainesville, FL.

Ellins, R.R. and R.R. Riesert, 1994. Tracing subterranean flow patterns in the Santa Fe River basin, Florida, with ^{226}Ra . *Hydrologic processes*, in press.

Ellins, R.R., Riesert, R.R., and R.R. Riesert, 1994. Hydrogeology of the eastern Santa Fe River basin. *Field Trip notes, South Eastern Geologic Society Spring Meeting*, Gainesville, FL.

Ellins, R.R., R. Riesert, R.R., and R. Lee, 1993. Using ^{226}Ra to assess groundwater/surface discharge interactions in the Rio Grande de Meramec in Puerto Rico. *Journal of Hydrology*, 155:133-144.

Million, R.E., Hanchak, R.R., Gallegos-Aguilar, V., and R.R. Abbott, 1994. Using ^{35}Cl and ^{37}Ar to determine groundwater ages in streams. *Journal of Environmental Pollution*, in press.

Mininger, R.J., and M. Koops, 1989. Gas exchange in the New River River based on ^{35}Cl detection. *Journal of Geophysical Research Letters*, 16:461-464.

Mountain, R.E., Headley, J.A., TCE, and L. Turner, 1987. ^{35}Cl and ^{37}Ar in Florida's Rivers and Lakes. *unpublished.*

Mountain, R.E., 1973. Geohydrology of the cross-fluoride springs canal area with special reference to the Gadsden County: U.S. Geological Survey Map 1-433, p. 117.

Mountain, R.E., and G.C. Petton, 1986. Water Resources of Florida: Fluoride, Fluorite, Fluorite.

Peterson, G.M., 1984. Applied Hydrogeology. Columbus, OH: Merrill Publishing Co.

Plummer, N.L., 1966. A note on the one-dimensional dispersion model. *International Journal Air Water Pollution*, 1st 611-618.

Fluoride Geological Survey, 1990. Florida's water quality monitoring process hydrogeological study. Florida Geological Survey Special Publication 34, Tallahassee, FL, 344 p.

Port, R.C., and R.S. Bear, 1978. the development of drainage zone systems in the dissolution of limestones and dolomites. *Canadian Journal Earth Sciences*, 15:1763-1779.

Port, R.C., and P.W. Milligan, 1987. Recent Geomorphology and Hydrology. London, Davis-Poynter, p. 322.

Port, R.C., Schubert, J., Mountain, R.E., Lyons, R.L., and R. Headley, 1975. Accumulation and elimination capacity of four different Florida stream discharge systems in Bimini Hill (Apalachee Highlands). *International Institute and Technology*, 16713-1684.

Porter, R.C., Schubert, R.P., and R.P. Headley, 1979. Determination of gas exchange ratios for a small stream in Walker Branch, Tennessee. *Water Resources Research*, 15(5):2305-2316.

Carneyay and Miller, Inc. 1992. *Watershed, Computer-Aided Design Software for Ground-Water Modeling*. J.W. Carneyay, Gainesville, FL.

Chamber, R.H., 1977. Groundwater in the Florida Straits, by Tolosa, J.H., and F.L. Segle, eds., *Proceedings of the 1976 International Congress on Coastal Hydrogeology*, Gainesville, Fla. University of Gainesville, Gainesville, 219 pp., p. 213-226.

Chad, J.R., 1944. Transverse mixing of dye along selected Lake Ontario oil flow, U.S.G.S. Water Supply Paper 1346.

Cooley, R.L., and R. Koenigsmark, 1980. Comparison of various methods and predictive equations for determination of extreme precipitation contributions on three small subwatersheds in Wisconsin. U.S. Geological Survey Water Resources Investigation 1980-001, 41 p.

Conrad, A., 1914. Der hydrographischezyklus in Europa. In: Giese, Berlin, 1912-1913. (partly translated to English 1982), p. 54-68.

Davis, J., 1962. *Soil Processes and Forest Landforms*. Int. Thompson, S. ed., Soil Processes, New York, 200 pp. Wiley & Sons Ltd., p. 343-431.

Desper, R.J., and C.R. Coffin, 1988. Management and assessment conditions for selected Florida streams. U.S. Geological Survey Water Resources Investigation Report 88-4008, 41 p.

Hoover, R.H., & Bush, R., 1975. Major groundwater processes in the evolution of carbonate-sedimentary systems. *Journal of Hydrology*, 24(1975):1-12.

Kincaid, Jean A., 1985. A Florida karst drainage system: hydrogeology and hydrography of the continental sheet west of Florida. Geological Society of America Abstracts with Programs, 17:162.

Kinn, J.D., 1981. Study and interpretation of the chemical characteristics of natural waters. U.S. Geological Survey Water Supply Paper 1854, 384 p.

Knott, R.H., 1986. Hydrogeology and water budget analysis of two limestone prairie, Big Bend State Biological Preserve, Levy County, North Carolina, U.S. Shantz. U.S. Geological Survey University, 184 p.

Minard, R.R. and R.R. Kinsler, 1983. Interpretation of the groundwater flow path of the Santa Fe River, Florida. *Water Resources Bulletin*, 19 (part 2).

Munn, J.B. and R.F. Beck, 1983. Water resources of the Santa Fe River Basin, Florida. U.S. Geological Survey Water Resources Investigations Report 83-4813, 100 p.

Nease, W.H., and A.P. Gandy, 1988. Atmospheric reconnection in a simulated storm. *Journal Geophysical Research-Atmospheres* 93 (15A-15) 1319-1344.

Gandy, A.P. Jr., R.F. Simpson, R. Perkins and T. Torrence, 1979. Analysis of groundwater and surface water-supply interrelationships in the Upper Oklawaha River Basin area, National Water-121 as a guide. John Muir Foundation, New York.

Johnson, R.E., Hanson, R., Beekman, A., Dohal, M., Evans, R., and P. Lerner, 1987. On the percolative infiltration of air-water gas exchange. *Journal of Geophysical Research*, 92 (15A-15) 1345.

Jennings, T.M., 1975. Bed-line porosimetry as a morphometric tool: New Bedford example. U.S. Geographer, 21:16-28.

Jennings, T.M., 1983. New Bedford. American Scientist, 71 (1):16-30.

Johnson, R.E., and R.R. Perkins, 1983. Use of the neutron probe to study gas transport in the West Fork Trinity River, Texas. U.S. Geological Survey Water Supply Paper 2094, 18 p.

Jordan, G.P., 1984. Large variations in viscosity of Florida. *Florida Association of Petroleum Geologists Bulletin*, 70 (10):11-1417.

Jordan, G.P., Bellamy, R.T., and J.W. Bedford, 1984. Petrology and geology of Pensacola Formation, Florida. *Petroleum Geology*, 1:197-198.

Kelvin, R., 1983. *Gas Phase Chromatography*. Blackie, Butterworth 220.

Kinsler, R.R., 1978. Hydrogeology of the Upper Floridan Aquifer, Florida. U.S.G.S. Water-Resources Investigations Report 78-1094, 11 p.

Kinsler, R.R., 1987. *Gas Chromatography*. Butterworth, Heinemann Publishing Company.

Rey, R.H., 1992. Examination of physical and geochemical water mixing processes using Radon-222 and Radon-220. Ph.D. Dissertation, Texas A&M University.

Richpatrick, P.A., Battaglia, R.J., Detmers, R., Parker, R.M., and L.L. De Long, 1989. Determination of stream generation and dilution by use of tracers. Techniques of water resource investigations of the United States Geological Survey, Chapter A18.

Rivard, W.R., 1988. Groundwater and surface water relationships in the Glassy Springs Area, High Sierras, El Dorado County, California. Ph.D. Thesis, Sacramento, California.

Rundtow, L.P. and G.D. Prestwich, 1987. U.S.G.S. Two-dimensional solute transport model (2D), National Research Institute, Water University, Indianapolis, IN.

Runkel, R.A., and G.T. Orlob, 1983. Turbulent dispersion and the generation coefficient. *Transactions of the American Civil Engineers*, 109(190-191).

Russek, J.M. and T.P. Fung, 1979. Development of a modified tracer technique for measuring stream generation rates. US ESRIC, National Technology Information Service, Springfield, VA.

Schofield, W.B., and R.L. Davis, 1987. The generation capacity of streams. U.S. Geological Society Survey Circular 844.

Sherman, G.L., Mathews, R.C. and R. Battaglia, 1987. Streamflow influences on physical and chemical features of a mountain stream. *Groundwater*, 26(216-221).

Swanson, J.B., 1984. The variation of the gas transfer coefficient with molecular diffusivity. In: *Gas Transfer at Water Surfaces*, Battaglia, R. and G.L. Sherman, (eds.), Kluwer N.V., D. Reidel, p. 253-263.

Swanson, J.B., 1984. Mixing experiments. U.S. NRC Planning Report No. 1, U.S. Planning Office for NRC, College Station, Texas, 85 p.

Swanson, J.B., and R.J. Wilson, 1988. The deliberately injected tracer for the study of dispersion mixing in the ocean. In: J.C.J. Kiliaan and R.M. Smart (eds.), *Small-scale Turbulence and Mixing in the Ocean*, Elsevier, Amsterdam.

Goodwill, J.R., R.J. Wallace, and W.B. Broadhead, 1990. A delineative tracer experiment in Santa Fe River Basin, Florida, 1031200-020.

Good, R.W., and R.P. Mollingsay, 1991. Radio measurements to estimate the delineation location and magnitude of groundwater storage. In: *Ground Water, Vol. 1, Ed. 1*, Federal Geomorphology, United States, 1991, p. 241-269.

Goodwill, J.R., and R.W. Luskowski, 1979. Hydrogeology and Hydrology of Rivers. In: *Geology, A. and Geomorphology, Hydrogeology of Florida Rivers*, Baskaran, R. (Ed.), International Association of Hydrogeologists, P-43-43.

Haas, J.W., 1988. Freshwater heads and groundwater temperatures in aquifers of the Northern Great Plains in parts of Montana, North Dakota, and Wyoming. U.S.G.S. Professional Paper 1400-Q, 11 p.

Leake, C.H., and R.L. Farley, 1992. Isotopic tracers for atmospheric moisture. *Atmospheric Environment*, 26:1563-1571.

Lee, G.H.T., T.L. Lee, and M.J. Hall, 1993. Two-dimensional mixing in rivers with randomly partitioned sources. *Journal of Environmental Engineering*, 119(1):145-149.

Lyon, P.L., McElroy, J., Goss, G.R., Stanley, P.R., Keppler, R.L., and J.C. Colantonio, 1979. Long term toxicity of four fluorescent brightening agents. *Food and Cosmetic Toxicology*, 17:621-627.

MacDonald, R., 1988. Geologic interpretation of the Florida Aquifer pollution potential in Alachua County, Florida. Florida Geological Survey, Open-File Report 88-1.

Malley, R.J., and R.L. Farley, 1990. Geomorphology and geologic structure of Florida. Geological Society of America Bulletin, 101:1813-1870.

McKee, R.L., 1991. Hydrogeologic surface of the upper Florida Aquifer in the Suwannee River Water Management District, Florida. Open-File Report 91-048, U.S. Geological Survey.

McKee, R.L., and C.R. Peart, 1991. Ground water modeling, northern Weber Hall, Association, 44 p.

Reiter, F.W., 1963. Reconnaissance of the geology and groundwater resources of Collier County, Florida. Florida Geological Survey Report of Investigations no. 16, 74 p.

Miller, J.A., Hughes, G.A., Hall, R.W., Vandekar, J., and P.R. Radke, 1988. Impact of potential phosphate mining on the hydrology of Cypress National Forest, Florida. United States Geological Survey, Water Resources Investigations 78-01.

Miller, R.L., and C.P. Cessna, 1990. Wetlands hydrology. New York, Van Nostrand Reinhold.

Hall, R.W., Moberg, T.B., Scott, J.E., and G.R. Meesing, Jr., 1988. Application of dye-tracing techniques for determining solute-transport characteristics of ground water in karst terrains. Environmental Protection Agency Report 600/R-88-081, 162 p.

Hall, R.W., Vandekar, J., and A.C. Rice, 1989. Catastrophic collapse of the West Florida Carbonate Platform Margin. *Geology*, 17:187-190.

Moghekar, R., and V. Rajeswari, 1989. Recent research to determine saturation coefficients. *Water Resources*, 3(3):1289-1301.

O'Connor, G.P., and M.L. Johnson, 1976. Mechanism of percolation in natural streams. *Transactions American Civil Engineers*, 103:681-694.

Pringault, R., and R.R. Moore, 1979. Diffusion and decay of aquatic herbicides in flowing streams. *Journal of Hydrology*, 46:217-230.

Mayes, R.L., Moberg, T.B., Smith, G.L., Jones, R.W., and R.R. Pringault, 1984. Origin of the epigenetic salt at Florida-Georgia beach ridges in Florida and development of the Florida salt. *Geology*, 12:614-618.

Osman, M., Edwards, R.M., and J.W. Gibbs, 1994. Saltwater intrusion studies in streams. *International Journal of River and Water Pollution*, 8(3/4):487-496.

Padilla, R.M., and R.P. Mayes, 1977. Simulation of stream groundwater in a model river. Rep. 100-76-03, CERG-13, University of Texas at Austin.

Pringault, R., 1979. Geologic controls on saline characteristics in coastal areas. *J. Geology*, 87:79-93.

Starker, G.W., and R.L. Gray, 1971. A procedure for estimating retention coefficients for Pennsylvania streams. U.S. Geological Survey Water Resources Investigations Report 61-1441-1.

Starkman, J.O., and R.B. Ramsey, 1971. Correlation of precipitation into streams. *Journal Geophysical Research*, **76** (11), 6111-6114.

Stark, G.W., Starker, P.S., Garry, J.W., and D. Weidelt, 1987. Estimating retention coefficients. Florida Department of the Environment, 1986 Transactions of the American Geophysical Union, 67(1):126.

Perkin Elmer, 1986. Atomic Absorption Techniques Manual. New York, Elsevier.

Flurkey, R.C., Jr., 1960. The Northern and Middle Sections of Marion County, Florida. Florida Scientist, 23(4):287-345.

Gray, A.P., Weidelt, R.A., Turner, R.L., Whittel, R.A., and R.B. Garry, 1979. The range of water temperature fluctuations in the limestone waters of the central and southern Everglades. *Journal of Hydrology*, 41:237-252.

Flake, D.J., and R. Friedman, 1994. *Introduction to open-channel flow. The Treatment, W. and R. Co. edn.*, The Transfer of Water Resources. Boston, Birkhäuser Publishing Inc., p. 229-246.

Florin, P. 1985. Sediment-geochemical studies of limestone and the Boulder Creek under the northeastern Florida continental shelf. Geological Society of America *Meetings with Programs*, 17:123.

Friedel, R.L., 1975. Summary of the development of basin topography. in: Weidelt, R.A. and Friedel, R.L. (eds.), *Therm of Landfill Development*. Ringwood, p. 227-242.

Friedel, R.L., 1987. *Hydrogeology and motion of the Ocala Group*. Florida Geological Survey Bulletin 89, 149 p.

Quinton, J.P., 1987. Qualitative water-tracing with dye in karst aquifers. In: Quinton, J.P., et., *Practical Karst Hydrogeology, with emphasis on Groundwater Monitoring* (series manual); Dublin, OH, National Water Well Association, Vol. 4, p. 31-324.

Bardossy, A.P., and J.H. Stone, 1986. Mass-action analysis using the tracer-augmentation technique of a modern aquifer. *Sedimentary Geology*, 49:309-323.

Batthauer, B.H., Stephens, D.M., Shadoff, D.R., and G.R. Mai, 1978. Laboratory studies of dye tracers for measuring streamflow coefficients. *Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers*, 104(EE1):326-336.

Batthauer, B.H., 1978. Estimating flow and dye quantities for modified tracer technique measurements of streamflow coefficients. *Water Resources Investigations Report*, 78-017-48.

Boggs, R.Q., 1974. Physical behavior and geologic control of solutes in mountain streams. Geological Bulletin no. 1010-01, U.S. Geological Survey.

Brown, T.E., 1986. The lithostratigraphy of the northern Apalachicola and Florida. Florida Geological Survey, Map Series 113.

Galvin, R.W., 1965. The underground course of the Santa Fe River near High Springs Florida. Master's Thesis, University of Florida.

Hunt, P.L., 1981. A review of the toxicity of twelve fluorescent dyes used for water tracing. *National Speleological Society Bulletin*, 48(2):119-130.

Hutchinson, T.B., and J.M. Johnson, 1986. Investigation of the possible formation of methyltin minerals resulting from the use of rottene or dye as a tracer in river waters. U.S. Geological Survey Water Supply Paper 2300, p. 10-18.

Howard, R.W., and R.R. Phelps, 1983. A study of the geochemical and natural purification of the Calo River, FL. Factors controlling the phenomena of oxidation and reduction. U.S. Public Health Service, Public Health Bulletin no. 144, Washington, DC.

Stringfield, T.P., Rapp, and B. Anders, 1979. Effects of bedrock and geochemical structures on the circulation of water and permeability in mountain aquifers. *Journal of Hydrology*, 43:211-233.

Talvagno, R.C. 1987. Dye tracer measurement of stream permeability. Federal Water Pollution Control Administration Report, Washington DC, U.S.

DeLoach, R.C., O'Connell, R.H., Walker, C.H., Redden, P., and G.R. Langford, 1984. Chemical characteristics of atmospheric precipitation. I. Laboratory studies. *Journal Water Pollution Control Federation*, 37(10):1243-1262.

DeLoach, R.C., and L.R. Barnes, 1986. Substratum response of the *Platida* encrustants, eastern half of Florida (abs.). *Meeting of Florida Palaeontologists and Mineralogists Annual Midyear meeting Jacksonville*, 3(1):12.

Hanson, R.O., 1973. Geology of Citrus and Levy Counties, Florida. *Florida Geological Survey Bulletin* 33.

Hedgpeth, J.C., 1971. Origin and development of limestone caves. *Progress in Physical Geography*, 5(3):340-354.

Huang, H.-P., and R.P. Anderson, 2000. Contribution to groundwater modeling-calcite difference and Florida limestone methods. San Francisco, CA, R.R. Prentice and Company, 337 p.

Kennard, R.R., 1988. Gas exchange across the air-water interface determined with natural and artificial bubbles. Ph.D. Dissertation, California University.

Kennard, R.R., Lebedeva, J.R., and R.H. DeLoach, 2000. Gas exchange wind speed relation with Walker limestone on a lake, Science, 287:1294-1296.

Kennard, R.R., Lebedeva, J.R., DeLoach, R.H., and R. Riedel, 1997. Gas exchange-wind speed relationship in Mono and Crowley Lakes, California. *Journal of Geophysical Research*, 102:14877-14888.

Kennard, R.R., McMichael P.J., and J.W. Elcock, 1996. Gas exchange across the air-water interface determined with dolomite and natural bubbles. *Water Resources Research*, 32:3683-3690.

White, W.H., 1986. Some geochemical features of central peninsular Florida. *Florida Geological Survey, Geological Bulletin*, 45(1):1.

White, W.H., 1990. Surface and near-surface karst landscapes. *Geological Society of America, Special Paper* 250, p.127-179.

White, W.H., 1994. *Geochronology and Hydrology of Karst Disseminations*. New York, Oxford University Press.

WILCOX, R.J., 1984. Restoration studies on some New Zealand rivers using methyl methacrylate as a tracer tracer. *Ph.D. Thesis*, N. and S. J. Jinks (eds.), *the Tressler of Water Resources, Rutherford, N.J.*, 9, 933-939.

WILCOX, R.J., 1988. Study of river restoration at different flow rates. *Journal of Environmental Engineering*, 114(8):120-125.

WILLIAMS, K.E., WILCOX, R.J., and A.R. BANISTER, 1977. The hydrology of the western part of Pinellas County, Florida. *Florida Geological Survey, Report of Investigation 50*.

WILLIAMS, P.M., 1972. Morphometric analysis of polypetal herbs in New Orleans. *Bulletin Geological Society America*, 83(780):780.

WILLIAMS, P.M., 1980. The role of subterranean trees in karst hydrology. *Journal of Hydrology*, 43:485-501.

WILSON, R.P., and G.M. HODGKIN, 1963. The use of sulfur hexafluoride as a conservative tracer in saturated sandy soils. *Ground Water*, 1(1):719-726.

WILSON, R.P., H.G. FLATHER, and R.M. HOGG, 1970. Sulfur hexafluoride as a tracer between River Between, Bronx City, New York, and Flushing, Long Island, U.S. Geological Survey Water Supply Paper 1966-C, 38 pp.

WILSON, R., STADLER, G.A., and G.M. JINKS, 1984. Assessment of a steady-state propane-gas tracer method for determining translocation coefficients, Chemung River, New York. *U.S. Geological Survey Water Resources Investigations Report 84-4016*, 49 p.

Biographical Sketch

Richard A. Knott was born by Gerald E. Knott and Nancy H. Knott on December 15, 1948 in the small, upstate town of Cobleskill, New York. He graduated from Cobleskill High School in 1966. He attended Herkimer College in Herkimer, Ohio, where he received his Bachelor of Science degree in Geology in 1968 while teaching and supervising the second year for four years. He then obtained his Masters of Science degree at Old Dominion University in Norfolk, Virginia, in the Fall of 1970. While attending Old Dominion University he worked at the University's Applied Marine Research Laboratory as a research investigator and hydrogeologist. In addition, he worked with The Nature Conservancy on his masters thesis in the Outer Banks of North Carolina. In the Fall of 1970 he attended the University of Florida while attending the University of Florida he worked as a teaching assistant, research assistant, and athletic tutor. Over the last two years he has worked with consulting firms in Jacksonville, Florida, as a hydrogeologist. He was married to Brook E. Tracy on September 21, 1968 and July 10, 1973.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Douglas L. Baldwin, Chair
Professor of Theology

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



George J. Gardner
Associate Professor of Theology

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Donald V. Gangel
Associate Professor of Theology

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



C. Marvin Hunt
Professor of Environmental Engineering
Technology

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Joseph A. Mirek
Associate Professor of Theology

This dissertation was submitted to the graduate faculty of the Department of Theology in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Dean, "Synthesis" Thesis